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THE CONSTANCY OF THERMOELEMENTS.

By Walter P. White.

ELECTRICAL thermometers are coming more and more into use, not only for the measurement of extreme temperatures and other special work, but even to secure for calorimetry an instrument superior to the mercury thermometer. Among electrical thermometers the resistance thermometer, for temperatures below 1000°, has been the one mainly used where accuracy and great sensitiveness were especially desired. The possibilities of the thermoelement in these directions have therefore remained comparatively undeveloped, while the great advantages which it frequently offers for particular kinds of work have been attainable only by the sacrifice of exactness. Palmer,[1] however, has already shown that the thermoelement may become an instrument of precision comparable with the best thermometers of other types; and the attainment of similar results in other cases is a matter of no great difficulty.

The errors of the thermoelement are almost entirely due to a single cause, inhomogeneity, which renders parasitic electromotive forces liable to occur at any point along the wires, and makes the reading of the element subject to change with every temperature fluctuation throughout its length. Where the trouble is due to a change in the material of the wires, it can generally be prevented by care in using the element. The inhomogeneity of the original materials can usually be diminished by making a proper selection of wires, or corrected by suitable treatment afterwards, and the

[1] A DeForest Palmer, Phys. Rev., 21, p. 65, 1905.

detrimental effect of what remains can always be reduced by various devices.

The effect of inhomogeneities can easily be expressed by an extension of the ordinary formula, which gives the electromotive force of homogeneous thermoelements. In any metallic circuit, let J be the junction between E and F, two portions of wire, each homogeneous in itself but differing from the other in thermoelectric power by an amount, $\triangle H$. Suppose the middle points of E and F cooled to the same temperature, θ_0, which may be as low as convenient. This cooling will not affect the thermoelectromotive force in the circuit, since it occurs within homogeneous portions of wire. If the temperature of J is θ_J there will be a thermoelectromotive force between E and F equal to $(\theta_J - \theta_0)\triangle H$.[1] A similar expression obtains for every other point in the circuit at which there is a change in H. The total electromotive force therefore equals

$$\Sigma(\theta_J - \theta_0)\triangle H. \tag{1}$$

Since the temperature θ_0 may be anything we please, it can be taken equal to 0, and equation (1) becomes

$$E = \Sigma\theta_J\triangle H. \tag{2}$$

In general, the variation in thermoelectromotive power along the circuit will be continuous. E and F may then be taken to be infinitesimal; the portion cooled to the temperature θ may be a second order infinitesimal (since the length of the cooled portion does not affect the thermoelectromotive force), and (2) becomes

$$E = \int \theta dH, \tag{3}$$

where the integration is to be carried over the whole circuit. dH of course is itself a function of θ.

The magnitude of the error due to inhomogeneity in any given case can easily be computed in accordance with formula (3) by a graphical method. This is illustrated in the following discussion of a contaminated platinum thermoelement in an electric furnace. The upper curve (LMN) gives the observed temperature gradient;[1] the next (PQR), the approximate thermoelectric power

[1] H, as here used, is strictly the mean thermoelectric power, a function of the temperature interval.

along the platinum wire of the thermoelement, which was also obtained by actual measurement. The wire, as the curve itself clearly shows, was considerably altered near the hot junction. OK is the thermoelectric power of the platinum-rhodium wire which formed the other branch of this element. OK is, therefore, the thermoelectric power which would have existed at the junction had there been no contamination. In order to represent graphically the

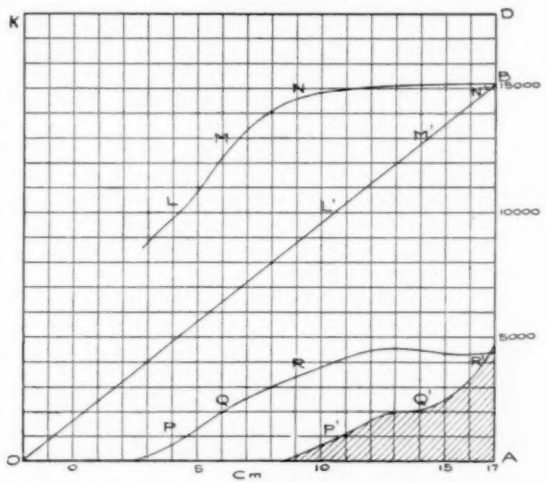


Fig. 1. Graphical method of computing the E.M.F. of an inhomogeneous element, applied to a platinum thermoelement in a resistance furnace. Upper curve, furnace temperature in microvolts (10 microvolts = approx. 1°), with depth in the furnace for abscissa; middle curve, thermoelectric power of the wire, arbitrary ordinate, same abscissa. Lower curve, same thermoelectric power, with temperature as abscissa. Total area, normal E.M.F., shaded area, error.

product θdH, the coördinates should preferably be θ and H; that is, the thermoelectric power should be plotted as a function of temperature and not of length. The required change of coördinates is effected by the following device: The line OB is drawn with B equal to the ordinate of the maximum temperature on the diagram. The temperature curve is projected horizontally upon this line, L, M, N of the curve falling at L', M', N'. The abscissæ of L', M', N' are now proportional to their ordinates (since they lie on a straight line through the origin) and are, therefore, proportional to the tem-

[1] The furnace was of the type described by A. L. Day and E. T. Allen, PHYS. REV., 19, p. 184, 1904; Carnegie Institution Publication, No. 31, p. 25, 1905.

peratures. The thermoelectric power curve is next shifted horizontally so that all the abscissæ are altered by the same amount as in shifting the curve L, M, N. For instance, if P, Q, R, were originally under L, M, N, they will be moved to P', Q', R', under L', M', N'. In practice, this shifting is easily done, and consists simply in taking with a pair of dividers PP' equal to LL', QQ' equal to MM', etc. The abscissæ of the curve P', Q', R', being the same as those of L', M', N', are likewise proportional to the temperatures. The curve P', Q', R', therefore, has its abscissæ proportional to the temperature and its ordinates to the thermoelectric power. The area $OADK$ represents the thermoelectromotive force which would be given by a thermoelement of homogeneous wires whose junction was at the temperature OK. The actual electromotive force is given by the area O, P', Q', R', D, K, and the lowering of electromotive force due to contamination of the wire, by the approximately triangular shaded area P', Q', R', A.

In this particular case, the effective thermoelectric power at the junction was about two thirds the normal, yet the reading of the thermoelement was lowered less than five per cent. The reason for this is, of course, that the contamination lay mainly in the region of uniform temperature, so that the maximum heat of the furnace extended out to a point where the difference in thermoelectric power between corresponding points of the two wires was much greater than at the junction. On the other hand, a small amount of contamination extending far from the junction evidently has a relatively great effect on the reading of the thermoelement — a point of importance in work with platinum thermoelements at high temperatures.

The reading of an inhomogeneous thermoelement is a function of all the temperatures throughout its length. In many cases where alterations in thermoelements have been reported, the effect observed was probaby due to change in the distribution of temperature along a really unaltered element.

Since the errors of thermoelements depend upon the intermediate temperatures, their constancy can be increased by increasing that of the temperature distribution between the junctions.[1] This is one of the ways in which the effect of an unavoidable inhomogeneity

[1] Holborn and Day, Drud. Ann., 2, 538; Am. Journ. Sci., 10, 197, 1900.

can be diminished. Of course, the element should then be calibrated for the particular temperature distribution with which it is to be used.[1]

On the other hand, the behavior of an element which has been used with a constant temperature gradient affords no criterion of the excellence of that element under less favorable conditions.

The errors due to inhomogeneity in thermoelements are sometimes, but incorrectly, spoken of as due to "Thomson currents." This doubtless arises from the fact that these errors are attributable to the middle and not to the ends of the wire. The Thomson effect, however, does not depend at all upon the heterogeneity of the wire, while the errors we have been discussing are directly due to it. Indeed, for most purposes it is convenient to think of an inhomogeneous theremoelement as composed of a number of short, weak elements in series.

Thermoelectric Testing of Wires. — The most satisfactory way to improve thermoelements is obviously to get rid of the inhomogeneity as far as possible, and such was the object mainly in view during the following work. In this attempt, the careful testing of the thermoelectric power of wires was important, either for study of their properties and behavior, or to control the selection and arrangement of the materials from which the thermoelements were made. Several types of thermoelectric wire testers were therefore made.

The thermoelectric properties of wires have usually been tested by moving some source of heat or cold along them — a Bunsen flame, for example, or a lump of ice.[2] This method has the advantage of simplicity, and usually shows the presence of inhomogeneity well enough. It seemed ill adapted to the quantitative work here described, for the following reason: In a thermoelement as ordinarily used, the electromotive force is not affected by any parts of the circuit which are at uniform temperature, but depends upon the difference in thermoelectric power of two wires, each of which passes from a hot to a cold region. Similarly, when a single wire is heated at one place, the portions which contribute to the result-

[1] The deterioration of contaminated thermoelements is often given in degrees. Of course, any such statement is meaningless unless something is said or implied as to the conditions under which the element is to be read.

[2] Edwin H. Hall, L. L. Campbell and S. B. Serviss, Proc. Amer. Acad., 41, 559, 1906.

ing electromotive force are those which pass from hot to cold at the edges of the heated region, and this electromotive force, therefore, measures the difference in thermoelectric power of these two portions of wire through which the temperature gradients extend. If, now, the heating is by a Bunsen flame, the two gradients are very near each other. To get the difference between two distant portions of the wire many of the short-length observations must be combined. As the error of each measurement is usually large compared to the whole variation in the wire, the result obtained by adding a number of observations may easily be in error by more than its whole value. The differences between distant points of the wire, however, are precisely those which have the greatest effect on the reading of the element.

The common method was accordingly modified by disconnecting one end of the wire and completing the circuit through an auxiliary wire which touched the other somewhere within the heated portion. (Fig. 2.) The circuit then contained two temperature gradients, one on each wire, and by drawing the tested wire along, all portions of it could be compared with the same fixed portion of the other. A map of the whole wire could thus be made[1] and a comparison of any two portions would contain the errors of but two observations. The auxiliary wire should be of the same material as the one tested, since otherwise large electromotive forces are introduced, whose variation, even with slight fluctuations of temperature, may quite cover up the electro-motive forces due to the differences in thermoelectric power under investigation. The temperature gradient should be at least as short as the inhomogeneities to be located. This method succeeds best where the working difference in temperature is high, since the effect of temperature irregularities away from the testing point becomes less important. With an ordinary

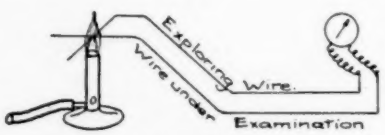


Fig. 2. Simple method of testing the thermoelectric height of a wire by means of a second exploring wire of the same material.

[1] As in Fig. 5 (in which, however, the comparison was with a fixed portion of the same wire). This curve corresponds to the integral of any one of the curves given by Hall Campbell and Serviss (loc. cit.).

Bunsen burner as source of heat, it proved excellent for studying platinum wires. A temperature of 1000° can easily be reached and kept constant within 2 per cent. A somewhat greater variation will do no harm if the wires are of the same material. Since the heating is done by a rapid current of air, the temperature gradient is sharp.

When the testing is done at ordinary temperatures, on the other hand, differences of temperature at other places on the test wire may cause disturbances. It is then better to use two exploring wires, one on each side of the temperature gradient, as in Fig. 3. The only portion of the inhomogeneous tested wire in the circuit is then the part (2 cm. or less) actually under examination. Freedom from disturbing electromotive forces will then be obtained if (1) the temperatures are constant, or (2) the exploring wires are homegeneous. As both these conditions can be nearly secured, this method gives excellent results. Most of the wire testers which were tried were constructed on this principle and differed mainly in the method of maintaining the temperature gradient. Steam was the source of heat. Ice was tried for the lower temperature, but was abandoned because it caused a condensation of moisture and thus endangered the insulation.

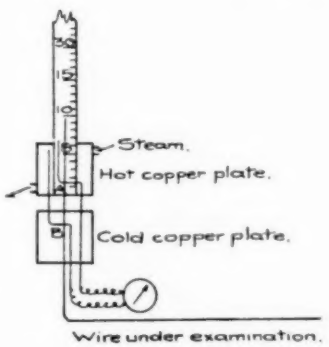


Fig. 3. Copper plate (dry) wire tester, using two exploring wires, making contact with the tested wire at *A* and *B*. The tested wire is drawn along the scale past the stationary exploring wires. Only two or three cm. of the tested wire is in circuit at one time, and all other wires exposed to temperature changes are of copper. A non-conducting pad covers the plates and wires when in use.

1. In the first form of tester, the wire ran from a hot to a cold globule of mercury. The results varied enormously with the condition of the surface of each metal. The temperature gradient was very sharp, but a sharp gradient was soon found to be seldom needed and to be obtainable by other methods ; hence this form of tester was abandoned.

2. By putting a ring of lead pipe carrying steam in the top of a jar of kerosene, a sharp gradient was obtained on account of the slow conduction of heat downward from the warm layer which formed at

the top. The thermal contact of the fluid with the wire was of course excellent. This device seems to have advantages where only a few tests are needed and the construction of anything elaborate is therefore undesirable; but it cannot be made as convenient as several other forms, and the initial temperature difference steadily diminishes.

3. A small, square, wooden box was set in an oblong tin can and the whole filled with kerosene. Two bodies of kerosene were thus provided, separated by a thin vertical partition of wood. Pipes carrying steam and tap water maintained the two at different temperatures and a propeller in each caused rapid motion of the fluid at the place where the wires ran through the partition. This apparatus gave a very sharp gradient[1] and great freedom in arranging and connecting the wires. It was of value in several cases, but for ordinary work a more convenient arrangement is possible.

4. In the wire tester with which most of the work to be described was done, the temperature gradient was maintained by contact of the wires with hot and cold plates of copper (Fig. 3). These plates formed the tops of metal boxes, through which flowed steam and tap water respectively. They were covered with shellacked paper to insulate them from the tested wires. The wires were laid on the plates and covered with a weighted pad, which at once pressed them firmly against the plates, insured good contact with the exploring wires, and checked the escape of heat upward. The temperature distribution in the wires, secured merely by contact with a solid substance, is probably not very uniform or regular, but any variation due to this cause in the small electromotive forces measured was too minute to be noticed. In fact, the apparatus was originally constructed so as to admit of using kerosene to make better thermal contact, but experience showed that the use of this disagreeable fluid was not necessary. Of course, the temperature of the wire need not be that of the steam so long as it is constant.

If the wire to be tested is insulated, exploring wires can not be used. For such cases, various pieces of apparatus were employed whose common principle is shown in Fig. 4, where E is an enclosure, maintained at a constant temperature by means of steam, through

[1] Ninety-five per cent. of the temperature difference was within 1 cm. with platinum wires .6 mm. in diameter (No. 22).

which runs the wire in such a way that any two portions of it may simultaneously be subjected to the temperature gradient at the edge of the enclosure, and thus compared directly with each other. If one point of the wire, *F*, is kept always at the edge, it can be com-

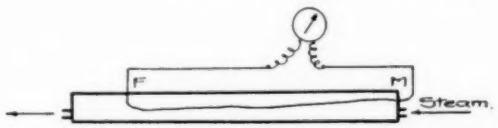


Fig. 4. Flat can wire tester. Adapted to insulated wires. The thermoelectric heights of any two portions, *F* and *M*, of the wire can be *directly* compared, and with almost no bending. A pad covers the wire when the test is made, or the wire may be inclosed between two similar cans.

pared in turn with all other points. The only essentials are that the temperature of the enclosure shall be constant and the length of wire within it capable of variation. It will not do, for example, to run the wire through a straight tube, since this requires heating a constant length of wire. The wire, however, if sufficiently flexible, can be doubled inside of a tube, when *F* and *M* will be near together at the same end. An apparatus of universal application is shown in Fig. 4. It consists simply of a long steam-heated metal case, flat on one side, against which lies the wire, covered by a thick pad of cloth. The temperature under such a pad is more uniform than that observed inside a steam-jacketed tube 14 mm. wide, and the adaptability of the method is obvious. This particular apparatus was not actually constructed, as the fine wires examined could be readily handled in tubes which we already had, but the constancy of temperature under a pad was measured carefully by means of a steam-heated varnish can. Such a can, or a flask, which can be set up almost at a moment's notice, makes a good substitute for the long metal case when the wire under examination is short.

Two types of thermoelements, one platin-rhodium, the other, constantan-copper, have been studied, with the result of improving considerably the accuracy of each.

1. *Platin-Rhodium Thermoelements.* — At the temperature of 1000° the platinum resistance thermometer begins to suffer a loss of accuracy. From that temperature up to 1600°, therefore, the thermoelement is the only satisfactory sensitive pyrometer available. Thermoelements made for high temperature work are now

tolerably familiar. Ordinarily they consist of a wire of very pure platinum, .6 mm. in diameter, joined by fusion to a wire of platinum alloyed with (10 per cent. of) rhodium or iridium. Couples containing iridium are the more sensitive at low temperatures. Their calibration curve is nearly linear. At higher temperatures, those alloyed with rhodium are nearly as sensitive and much more constant. They were the only ones studied. Connected to a voltmeter, these thermoelements form a direct-reading, convenient and accurate pyrometer of wide range. When read by means of a potentiometer, they are capable of much greater accuracy. One pair of elements has been carefully studied as far as 1000° and has never shown a disagreement greater than one half microvolt, corresponding to about $\frac{1}{2}\frac{1}{0}$° at the higher temperatures, and other elements have usually given results almost equally good as high as 1500°.

The principal problem presented by our thermoelements was the rather unusual one of preventing a rapid and continuous alteration of the wires when in use.

It has long been known that the reading of platinum thermoelements and resistance thermometers is easily altered at high temperatures by contamination of the metal. As far as observed until recently, the trouble always occurred in a reducing atmosphere. Holborn and Wein [1] found that hydrogen alone had no effect, but in the presence of silicates it liberated silicon, which attacked the platinum. Reducing gases containing carbon were also believed to be deleterious to thermoelements, but I have not been able to find satisfactory experimental confirmation of this view. Holborn and Day [2] subsequently found that furnaces made of fresh or imperfectly burned clay gave trouble, which was attributed to the organic matter contained in the clay. The contaminated wires were usually restored by igniting at high temperatures in the air, though it was frequently necessary to cut off portions of the element on account of impurities which could not be driven out in this way. The danger of contamination in an oxidizing atmosphere seems hitherto to have been considered negligible.

When work was begun in this laboratory, the methods used by

[1] Holborn and Wien, Wied. Ann., 56, 373, 379, 1895.
[2] Holborn and Day, loc. cit.

Holborn and Day at the Reichsanstalt were adopted, with some improvements calculated to adapt them for use at higher temperatures.[1] A platinum-iridium alloy replaced the platinum or nickel of the coils, and a new insulating material consisting mainly of magnesia was substituted for clay in the body of the furnaces. Rapid deterioration of the thermoelements at the higher temperatures was soon observed, the magnitude of which was altogether unexpected and for a long time defied explanation, as special precautions had been taken to avoid the presence of reducing matter in the furnaces. The possibilities of contamination through dissociation, electrolytic action, organic or ferruginous dust (both of which abounded in the laboratory), or the volatilization of iridium from the furnace coils, were all considered; but none of these explanations seemed to account for all the facts, and the further precautions which occurred to us, such as cleaning and ventilating the porcelain tubes surrounding the thermoelements, were without effect in remedying the trouble.

For a time, therefore, furnace work was conducted by means of a provisional arrangement. The working elements were used in their contaminated condition, but were compared frequently with standards which, being in the furnace only five or ten minutes each day, kept their values very well. The simplest way to compare the two thermoelements is, of course, to read both when at the same temperature. In an electric furnace of ordinary size, temperature gradients are so steep that the only satisfactory way to bring two junctions to the same temperature is to thrust both together into one of the porcelain tubes which are made for protecting thermoelements in furnaces. This can be done if each element has but one insulating capillary, leaving the other wire bare. If care is taken to keep the bare wires on opposite sides of the porcelain tube, the elements can be pushed down without crowding, and at the same time the capillary tubes will prevent the bare wires from coming in contact. No such contact has been observed in several hundred comparisons. The thermoelements thus located are read alternately and as rapidly as the galvanometer will allow. Change in the furnace temperature can easily be allowed for. Comparisons can also be made by

[1] Day and Allen, loc. cit.

putting one element after another into the same porcelain jacket, though not so well, since five minutes are required to attain temperature equilibrium after a cold element has been inserted in the jacket. Hence the furnace must previously be adjusted to constant temperature, which requires some time, and even then results are not very certain. Simultaneous readings of two elements in separate tubes are also unreliable at high temperatures, as equality of temperature can not be assured. In a furnace at 1400°, differences of 2° have been observed between similar tubes symmetrically placed and so close to each other as to be in contact through most of their length. By comparing two elements in two such tubes and then reversing and comparing again, the difference in temperature of the tubes can be eliminated and with excellent results. The conditions, however, must be such that the temperature difference remains constant.

The comparing of thermoelements has been of the greatest value in high temperature work. It may be used as a substitute for or check upon the tedious process of calibrating by means of metallic melting points; it affords a valuable control of the extensive extrapolation which is necessary above 1000°, and insures that results obtained with different elements at these higher temperatures shall be comparable among themselves; and it serves to indicate the first signs of deterioration. Applied to elements which are much contaminated, however, it has a disadvantage obvious in the light of the previous discussion (see p. 452), since the reading of the contaminated elements, being a function of the temperatures throughout the contaminated portions, varies with the condition of the furnace. In that work which we were forced to carry on for some months with contaminated elements, this difficulty was minimized by correcting the elements immediately after the temperature reading had been taken and in the same tube, so that the temperature gradient along the element might be as nearly as possible the same for both operations. The contaminated ends of the working element were also cut off as soon as they had fallen off 3 or 4°. By virtue of these precautions, measurements could, in favorable cases, be made to agree within .3° at 1400°. There was often, however, a good deal of uncertainty, which made the continual comparisons seem very irksome. We were finally driven to a consistent effort to get rid of the contamination altogether.

The systematic attack upon the problem began with an attempt to learn more of the actual condition of the contaminated elements. This study was begun by physical methods, the thermoelectromotive force of the wire furnishing a convenient and delicate means of investigation. Several of the wire testers described above were used, and contaminated elements were examined, centimeter by centimeter. The first day's work yielded results of importance and led to several surprises, in which conclusions derived from the experience of others and from our own occasional observations were found to be for the most part erroneous.

In the first place, the process of igniting the elements to free them from impurity was found to be practically useless, being almost without effect upon the contamination with which we were dealing. This practice, borrowed from the Reichsanstalt, had not seemed satisfactory, but whenever special failures were noticed, these had been attributed to a lack of thoroughness in the heating process.

Second, the thermoelectric height due to the contamination of the platinum wires proved many times greater than had been supposed. Immediately adjacent to the junctions, it was sometimes half that of the rhodium alloy of the other wire. The amount of alteration had previously been inferred from the change in the reading of the whole element when in the furnace, and thus, as is evident from the discussion of Fig. 1, above, too low an estimate had been made.

Third, a similar discovery was made regarding the rhodium alloyed wires. Nothing whatever appears to have been published upon this point; their contamination is considerably less than that of the pure platinum, and was therefore probably overlooked. The contaminating material was commonly believed to be subject to some selective absorption by which the platinum alone was affected. The tests, however, showed that the rhodium wires gained in thermoelectromotive power on the average one-fifth as much as the platinum. This information was especially important. The contamination had been supposed to be due to mere traces of foreign matter whose minuteness made the task of discovering and subsequently excluding them appear exceedingly difficult. The amount of impurity taken up by the rhodium wires, however, was evidently com-

parable to the amount of alloy (10 per cent.) initially present in them. The contaminating materials, therefore, were present in measurable quantities, and the prospect of identifying and then avoiding them appeared decidedly encouraging.

For this task, again, the wire testers were invaluable. They were capable of detecting an amount of impurity far beyond the reach of chemical analysis, and could work upon wires less than 2 cm. long. By subjecting short pieces of pure platinum wire to various possible sources of contamination, one after another, information could be obtained rapidly and at slight expense. When pure platinum wire was heated in our furnaces at 1400°, contamination occurred regularly and certainly, After an hour at this temperature, the resulting thermoelectromotive power (measured at 100°) was about 4 per cent. of that of the ten per cent. rhodium wire. One-third of a per cent. could readily be detected. There was therefore no question as to the possibility of recognizing the presence of any source of contamination similar to that existing in our furnaces.

1. The first possibly contaminating materials investigated were reducing gases containing carbon. Wires were heated directly in a blast flame and electrically in illuminating gas and carbon monoxid, to various temperatures up to the melting point of platinum, but no contamination whatever could be found. In this particular, our results fail to confirm the observation made by Holborn and Wien that while the contaminating action of hydrogen is due to the liberation of silicon, carbon alone may contaminate thermoelements.[1] Carbon, like hydrogen, appears to act simply as a reducing agent, and is detrimental only in the presence of other material which yields contaminating products on reduction.

2. A pure platinum wire was then suspended in a furnace without the customary porcelain protecting tube. The usual amount of contamination occurred. The results with gas had shown that the impurities came from the materials of the furnace; this experiment showed also that they reached the wire in the form of vapor. Among the volatile materials in the furnaces, iridium (from the heating coils) was the immediate object of suspicion. Our furnaces when hot were known to be filled with iridium vapor, which con-

[1] Loc. cit.

densed as a black deposit on the cooler portions of the furnace in quantities sufficient for chemical identification.

3. Further light on this subject was obtained through the kindness of Mr. George B. Hollister, of the Corning Glass Works, Corning, N. Y., who loaned us a thermoelement which had been in continuous use at 1400° for four months in a glass smelter, which was heated exclusively by gas. If iridium was really the cause of the contamination, this element might have been expected to remain unaltered. It showed contamination, though comparatively little, considering the length of time it had been in use. A striking peculiarity was, however, presented by the rhodium wire, whose thermoelectromotive height was not increased at all. The contamination of this element, therefore, was clearly due to a different cause from that of our own. Furthermore, the absence of contamination in the rhodium wire suggested that that wire itself probably furnished the only contaminating material to which the platinum wire could have been exposed. The properties of the two metals are such that if iridium vapor was capable of alloying platinum in an oxidizing atmosphere, rhodium would naturally be expected to produce a similar and smaller effect. Hence, in spite of the contaminated platinum wire, the condition of this element strengthened the belief that iridium was the impurity in our own thermoelements. One and one half per cent. of rhodium has since been found in the platinum wire of the Corning element by chemical analysis, but this result was not obtained until sometime afterward.

4. A direct test of the action of iridium was of course next in order. To make it, the platinum wire must first be heated in the absence of iridium. All our furnaces contained that metal, but a means of excluding its vapor was found in the use of glazed Marquardt tubes. These glazed tubes are not recommended for use above 1200°, but their deterioration at somewhat higher temperatures is very slow, and the one used in this work gave no indication of injury from overheating after five hours at 1500°. A platinum wire heated in this tube for an hour at about 1500° showed no contamination. When the experiment was repeated with a piece of iridium-alloyed furnace coil wire beside it in the same tube, there was contamination, and about as much as usually occurred in the furnace itself with the same time and temperature.

Platinum was therefore certain to become contaminated in the presence of iridium. Since, moreover, this change agreed in amount with that acquired in the furnace, and since porcelain, a silicate, caused no injury to the wire, the inference seemed justified that the non-metallic furnace materials had no share in producing the contamination, but that it was entirely due to iridium and rhodium.

5. Further confirmation of the above results by chemical analysis now seemed feasible and desirable. Dr. Eugene T. Allen, of this laboratory, undertook the analyses, both of a wire contaminated with iridium and of the one from the Corning Works, supposed to contain rhodium. In both cases the impurity sought was found in substantially the amount expected from the observed change in thermoelectric power. Dr. Allen's report follows.

The Detection and Estimation of Iridium and Rhodium in Thermo-elements. — For iridium, the method in its essential features was that of Deville and Stas. The platinum-iridium alloy is dissolved in ten times its weight of pure lead, by holding the two in contact for four hours or more at about 1000°. Most of the lead is then removed by dilute nitric acid and the spongy residue extracted with ten per cent. aqua regia. The iridium remains undissolved. Several test alloys prepared by fusing pure platinum and pure iridium (from Heraeus) with ten times their weight of lead, gave invariably high results, but when the lead was increased to twenty times the weight of the platinum metals, the result was satisfactory.

	Taken.	Found.
Pure lead,	10 + gr.	
" platinum,	0.5024 gr.	
" iridium,	0.0117 gr. iridium	.0121 gr.

Iridium in the platinum wire of an old thermoelement.

Taken.	Found.
9 cm. platinum wire, 0.4913 gr.	Iridium, .0076 gr. = 1.54 per cent.

The metal obtained gave the following tests characteristic of iridium :

1. Mixed with sodium chloride and heated in chlorine it slowly changed to the somewhat volatile, brown sodium iridium chloride which dissolved in water with a red brown color.

2. The solution in 1 gave with ammonium chloride the rather difficultly soluble, almost black ammonium iridium chloride.

3. On boiling with alcohol and caustic soda a blue solution of iridium trichloride was formed.

4. A small portion heated with ammonium nitrate and concentrated sulphuric acid gave a blue color.

The rhodium was estimated by the method of Deville and Stas, which consists in the solution of the metal (it should be previously rolled into thin ribbon) in aqua regia, precipitation of the bulk of the platinum by saturated ammonium chloride solution, separation of the rhodium with the remaining platinum from the filtrate by long boiling with ammonium formate, and final separation of the rhodium by fusing with acid potassium sulphate, from which it is precipitated in condition to weigh, by the action of ammonium formate. The method was tested on an alloy synthesized from pure platinum and the ten per cent. rhodium alloy of Heraeus.

	Taken.	Found.
Pure platinum,	0.4440 gr.	
10% rhodium wire,	.0241 gr.	
∴ rhodium =	.0024 gr.	rhodium — .0027 gr.

The filtrate from the ammonium platinum chloride, amounting to perhaps 20 cm.^{3}, was decidedly pink, and the color of the potassium acid sulphate fusion when hot was claret, yellow when cold. On trial it was found that one mg. of rhodium (in the form of potassium rhodium chloride [1]) in 10 cm.^{3} was distinctly pink.

Rhodium in the thermoelement.

Taken — platinum wire of element,		.4484 gr.
rhodium found,		.0033 gr.
	=	0.73 per cent.

The same color indications of rhodium were observed here in the filtrate from the ammonium platinum chloride and in the potassium acid sulphate fusion.

6. Although platinum wire was not injured in a gas flame, in the exhaust from a Fletcher gas furnace contamination occurred, as had, indeed, been expected. The cooler portions of the furnace

[1] The author is indebted to Dr. W. F. Hillebrand for a sample of this rhodium salt.

top were covered with a deposit of ferric oxide, which was so distributed as to show that iron in some form had almost certainly been brought up from the furnace by the escaping gas, oxidized, and deposited there. It therefore seemed quite probable that iron vapor, as well as silicon,[1] may be a contaminating material in furnaces containing a reducing atmosphere. This was confirmed by heating platinum as usual, at 1500°, in a glazed porcelain tube with a few milligrams of iron wire. Contamination resulted, although the two wires were not in contact.

7. An investigation of the behavior of iron in an oxidizing atmosphere was suggested by this last result. Ferric oxide heated as usual in a glazed porcelain tube with (but not touching) a fragment of platinum wire, failed to produce any contamination; thus strengthening the conclusion that non-metallic furnace materials are harmless in an oxidizing atmosphere.

Platinum, then, is subject to contamination at high temperatures by the vapor of iridium and rhodium, even when these are present in small quantities. The impurity is only slightly diminished by ignition in air. Besides these metals, and gold and silver, there seems to be no contaminating agency which need be feared in an oxidizing atmosphere. Commercial platinum always contains iridium, and its use within the furnace must either be avoided, if thermoelements are to be kept constant, or else some protecting arrangement, such as glazed porcelain tubes, be used. Unglazed tubes, except in metal work, are valuable only as a mechanical support. In any case, contamination of the platinum from the rhodium wire will take place, although with relative slowness. Good elements, therefore, should preferably be exposed to high temperatures for as short periods as possible. A reference to Fig. 1 shows that platinum does not become contaminated by iridium vapor below about 900°.

Thermoelements alloyed with iridium are known to be less constant than those with rhodium, and the difference has usually been attributed to the loss of iridium by evaporation from the alloy. In the light of what precedes there can be little doubt that it is due

[1] Shown to be a contaminating material by Holborn, Wien and Mylius. Holborn & Wien, loc. cit.

rather to the absorption of some of the iridium vapor by the platinum wire. If this is so, iridium elements should be more constant if used so that the platinum and the alloyed wires were not close to each other. On inquiry, it was found that Drs. Waidner and Burgess, of the National Bureau of Standards, in this city, had actually observed that iridium elements kept their calibration better when stretched directly through the furnace than when doubled at the junctions as usual.

Beside chemical composition, the hardness of a metal affects its thermoelectromotive force, and the platinum thermoelements are liable to a temporary error from this source. New elements are usually hard from the drawing of the wire, sometimes reading as much as two per cent. high at room temperature. If they are not annealed before use, the softening of the heated portions produces inhomogeneities, which are also liable to continual change on further heating. The wire may also become hard during use from bending or other mechanical strains incident to handling, and also perhaps as a result of the brittleness (crystallization) which platinum attains when heated to moderately high temperatures — a point deserving further investigation. Fortunately, the annealing of platinum wires is very easy, on account of the absence of oxidation, so that the hardness of a platinum thermoelement need never be regarded as other than temporary. In this laboratory, only that part of the wire which is to be in or near the furnace is usually annealed. A wire of the usual size, .6 mm. in diameter, will carry 17 amperes when freely suspended, while 15 amperes is more than sufficient to soften it. There need be, therefore, no danger of melting off the wire.

The chemical purity of the original material is less under the user's control than most other causes of inhomogeneity. It is fortunate, therefore, that the chemical homogeneity of the best platinum elements now on the market is practically perfect. The platinum and rhodium wires of two thermoelements were tested throughout their length of 150 cm. at 1000° by means of a Bunsen burner, in the manner described above (p. 454). No effect due to inhomogeneity was found as great as the accidental errors of observation, which were about one-hundredth of one per cent. of the

electromotive force of the element at that temperature. In ordinary use the temperature at any one point of the element would rarely vary 100° for the same temperature at the junction, and the error due to inhomogeneity would therefore not exceed .01°, which is considerably less than the usual error from other causes.

The last discussion suggests a point of some interest. The standard size of thermoelements (.6 mm.) was adopted after investigation by Holborn and Day, who found that finer wires did not give constant results. At that time, however, the contamination of platinum was not so well understood, nor the danger from hardening. It seems highly probable, therefore, considering the great homogeneity of thermoelement platinum, that considerably finer wires than .6 mm. would work perfectly well in very many cases. The main disadvantages would be the increased liability to contamination, and the greater danger from insufficient insulation, due to the higher resistance. Both these effects would decrease very rapidly with the temperature. The main advantages would be the lessened conductivity for heat and the reduced cost.

Any account of the present investigation would be incomplete which did not acknowledge its special indebtedness to the active interest of Dr. Arthur L. Day, of this laboratory.

II. *Copper Constantan Thermoelements.* — The second type of thermoelement investigated was of copper and constantan, and was intended for work at ordinary temperatures. The reasons for preferring a thermoelement to a resistance or mercury thermometer lay largely in the special conditions of the work for which they were to be used. The expectation of attaining greater ease and accuracy of reading than with a mercury thermometer has been abundantly confirmed.

The work of Hall, Campbell and Serviss,[1] and of Palmer[1] had apparently shown that an accuracy of .01°, for measurements up to 45°, could readily be obtained with commercial wire. Instead of a single thermoelement, five elements connected in series were used, enclosed side by side in a common tube, constituting what may perhaps be called a thermobattery. A double advantage was expected from this mode of construction: (1) The greater electromo-

[1] Loc. cit.

tive force made errors in the electric measurements less important, and (2) the accidental inhomogeneities in the wires would tend to neutralize each other. Insulated wire was, of course, needed, and copper was therefore substituted for the iron or steel commonly used. This change was considered an advantage, however, for another reason. Iron wire is notoriously uncertain in its thermoelectric properties, while copper is remarkably constant; hence, with wires of copper and constantan, there is only one-half the likelihood of trouble from inhomogeneity, and the electromotive force is still four-fifths as great as with constantan and iron. The constantan wire was No. 36 (.127 mm. diameter) obtained from the Driver-Harris Company, by whom it is sold under the trade name, "Advance." In order to control the accuracy of the results, two similar thermobatteries were made. Comparisons of these under various conditions showed that the readings were not constant, and that the trouble was probably due to inhomogeneity in the original material. An examination of some fresh wire from the same spool by means of a jacketed tube tester confirmed this suspicion. Three samples of wire, each 3 m. long, gave similar curves, one of which is shown in Fig. 5. The maximum variation is about .2 per cent. of the thermoelectromotive force against copper. This variation is evidently periodic. Mr. H. C. Dickinson, of the Bureau of Standards, in conversation, has mentioned finding inhomogeneities with a period of the same length, about 60 cm., in wire of a different size obtained from the same company. I am indebted to him for the suggestion that the periodicity of the inhomogeneity points strongly toward an origin in the annealing process, when the wire may have been in coils of 60 cm. circumference. It is inconceivable that the peculiar curve of Fig. 5 should itself be the result of chemical inhomogeneity, nor are there any other irregularities greater than .013 microvolt per degree which can be due to that cause. Probably the effect of chemical inhomogeneity is even less than that, and altogether negligible.

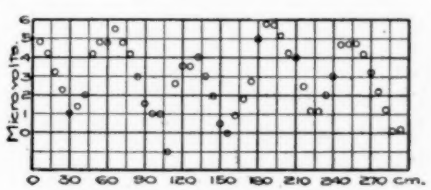


Fig. 5.

Better wire could, therefore, doubtless have been obtained by further search, but it seemed preferable to avoid delay by using that on hand, diminishing the effect of its irregularities by the method of construction. The device employed was the one already tried, of allowing the inhomogeneities to balance each other, except that instead of trusting to the chances of partial compensation among the numerous wires, the curve in Fig. 5 was used to select two lengths of wire which could be combined so that their variations were at every point nearly equal and opposite. The resultant thermoelectromotive power, as indicated by the curve, was then constant within .013 microvolt. The probability of error from inhomogeneity with the thermobatteries thus made can be estimated as follows: Whenever a thermoelement has received an individual calibration, the errors due to inhomogeneity depend, not upon the absolute values of the intermediate temperatures, but upon their variation from the condition prevailing during calibration. The results of the calibration will, therefore, include the effect of all temperatures which regularly vary with the junction, that is, of the temperatures of the portions near the junction, which are immersed in the bath with it. The variations of temperature which may accompany a given temperature at the junction are the only ones which can cause error. As the thermobattery here described was to be used with nearly constant immersion, the greatest variation of this sort was that of the portion exposed to the air, and was not greater than 20°. The maximum error was, therefore, $20 \times .013$, = (about) .25 microvolt, and since the thermoelectric power was 80 microvolts for a degree, this corresponded to an error of .003°. The result fully confirmed this estimate. Two such thermobatteries were made. Inclosed in the same tube they showed a permanent difference (which is not an error) of about .3 microvolt at 30°, which was about the limit of the sensitiveness of the galvanometer. The variation between the two was less than this, and altogether too small to measure. When both junctions of one were immersed in ice baths, the middle running through the air at about 30°, no variation from zero in the reading could be detected. With the two batteries in series, therefore, the error is not over .002°, and probably much less, as far as the batteries themselves are conerned.

These results are not markedly better than those reported by

Palmer, except for the increased sensitiveness gained by putting the elements in series. The method by which they were obtained, however, leaves the experimenter less dependent upon good fortune in getting originally homogeneous wire. Palmer does not appear to have considered the inhomogeneities of commercial wire at all important. The very experiment which is often used to investigate the quality of a thermoelement — that of reading it with both junctions in ice — he uses to show that the temperatures of the different ice baths were identical, and he does not mention inhomogeneity at all. His results, therefore, while they show something of the accuracy attainable with the thermoelement, appear to be misleading as to the ease with which that accuracy can ordinarily be obtained with commercial wire.[1] Their reproduction by another will be uncertain, if not improbable, without attention both to the quality and the treatment of the wire.

On the other hand, it should not be forgotten that the extreme refinement here considered is not always needed; sufficient accuracy for many kinds of work can usually be obtained with such simple precautions as are discussed immediately below.

The permanence of the thermobatteries seemed to depend npon three things. First, freedom from mechanical strain, the hardening effect of which is well known. Whether annealing is a satisfactory remedy in the case of constantan does not seem to be settled. With insulated wires it was, of course, out of the question.

Second, protection against chemical change, which in this case means oxidation. The effect of a layer of tarnish in altering the thermoelectric power of wires is also familiar. A number 22 constantan wire (.6 mm. in diameter) which had lain exposed to the air of a well ventilated laboratory for three months had its electromotive force against copper altered over .6 per cent.[2] This trouble can be corrected by scouring off the tarnish, but the restoration of the original electromotive force of the wire was not considered certain. Moreover, this remedy also was inapplicable to insulated wires.

[1] It will not do to infer from Palmer's results even the probable homogeneity of commercial wire, since three of his elements (page 75) differ .1 per cent. among themselves, indicating that there was somewhere in the wire a variation in thermoelectric power at least half as great as that shown in Fig. 5. That amount of inhomogeneity would often produce errors considerably greater than those he actually found.

[2] Elements of constantan and other base metals, therefore, will not maintain their accuracy at temperatures high enough to cause oxidation.

Third, preservation of the insulation, which meant, practically, protection against moisture.

All these requirements could have been secured well enough in ways which would have left the middle portion of the wires reasonably flexible. But since, for the work in hand, rigidity was not inconvenient, it seemed better to avoid all possibility of trouble, and the elements were accordingly completely inclosed in suitably bent glass tubes.

The outside diameter of the tube inclosing the hot junction of both batteries is 3.3 mm. at the end. The time lag is 3 seconds in gently stirred water. The resistance of each is about 30 ohms.

The permanence of constantan elements can also be increased in another way. Wire is less liable to vary if initially in the condition to which use tends to bring it. Just as elements used at high temperatures, where they are certain to become annealed in part, should be annealed throughout before calibration, so those liable to be irregularly hardened in handling become immune toward that cause of inhomogeneity if thoroughly hardened in the first place. Of course, the hardening must be uniform, and the possibility of making it so seemed worth a brief investigation.

The small insulated constantan wire was easily hardened by working it back and forth over the square corner of a piece of wood. Wires thus treated, after being "aged" by heating to 100° for 15 minutes (a precaution whose necessity was immediately discovered) were tested for thermoelectric power. The total electromotive force against copper had increased .8 per cent or .33 microvolt per degree, but the greatest variation along the wire was less than the experimental error, which was about .013 microvolt per degree. This uniformity was not dependent on uniform working of the wire, as long as the hardening was thorough. The wires seemed to rapidly approach a constant condition. This would naturally be anticipated, and is essential if the method of hardening is to have much practical value. An important further consequence of it is that any variations in hardness originally present will disappear as the wire approaches the uniform condition. Hardening, therefore, supplies a method of securing initial homogeneity as well as of increasing the permanence of the element in use.

The degree of homogeneity shown to exist depended upon the experimental error in the method of testing. A more careful examination would probably show that the actual homogeneity is considerably greater than that already demonstrated. Further investigation of this question, however, while desirable, has seemed more appropriate to a laboratory not especially equipped for work at high temperatures. The original object of the present investigation was secured by the construction of the pair of enclosed thermoelements already described. For the method of hardening wires, enough seems to have been done in calling attention to its value, and showing that it is already capable of producing homogeneous thermoelements whose errors scarcely exceed those of the electrical apparatus by means of which they are likely to be read.

Summary.

1. The main source of error in thermoelements is inhomogeneity, by the removal of which, in most cases, far greater accuracy may be attained than has hitherto been realized.

2. The electromotive force of an inhomogeneous element equals $\int \theta dH$, where θ is temperature, and H, the thermoelectric power. This formula can be applied by a convenient graphical method. The errors due to inhomogeneity depend on the temperature distribution along the element also; a change in this distribution therefore produces the same result as a further alteration in the element. Such errors can be made to decrease indefinitely as the temperatures remote from the junctions of the element are made more constant.

3. Thermoelectric wire testers, of several easily constructed types, proved invaluable in these studies and in the making of thermoelements.

4. The effect of initial chemical inhomogeneity is practically negligible, as far as thermoelement work is concerned, in (Heraeus's) thermoelement platinum wires, in commercial copper, and, often if not always, in constantan.

5. The effect of physical inhomogeneity — that is the variation in hardness — in these wires can by no means be neglected. New wires are usually hard drawn. This hardness, as well as that which may result from bending, etc., can be quickly and effectually removed from platinum wires by annealing. In constantan, a

thorough hardening also produces uniformity and leaves the metal nearly free from liability to further change through handling.

6. Constantan and copper wires are apt to become chemically inhomogeneous through the formation of a film of oxide or other tarnish. Even at ordinary temperatures and in well ventilated rooms, an error from this cause amounting to as much as one half per cent. may easily develop within a few months. Cleaning off this film nearly, if not quite, restores the original calibration.

7. Platinum at high temperatures takes up impurities which diffuse into the wire. Carbon, illuminating gas, etc., produce this result only through their reducing action on other substances capable of injuring the platinum — of which iron (which reaches the platinum in the form of vapor) and silicon are perhaps the most important. In an oxidizing atmosphere, silicates and iron oxides are harmless, but contamination occurs above 900° from the presence in the hot furnace of small quantities of rhodium, and especially iridium, either pure or in alloys with platinum. All of these metals are somewhat volatile at high temperatures. The contaminating impurity can not be removed, but can be excluded by inclosure in glazed Marquardt porcelain, which, moreover, is fairly durable at 1500°.

8. Where the use of contaminated elements is necessary, fair accuracy can still be obtained by frequent comparison with standards under conditions such that the temperature gradient along the contaminated wire is always the same.

9. Frequent comparisons of platinum elements are always desirable in order to control the calibration and the unavoidable extrapolation.

10. Thermoelements of platinum-rhodium, and of constantan-copper, when used with proper precautions, have been found free from any error as great as .005 per cent. With the platinum, this amounts to less than one twentieth degree at 1000°; with constantan, to less than .002° for measurements up to 40°. Furthermore, this result with constantan was obtained with rather inferior wire, by uniting elements in series in such a way that the variations along the wires counteracted each other.

GEOPHYSICAL LABORATORY,
CARNEGIE INSTITUTION OF WASHINGTON, D. C.,
September 21, 1906.

NOTE ON THE COMPARISON OF CAPACITIES.

By A. Trowbridge and A. H. Taylor.

IT has been pointed out by Rosa & Grover[1] that the capacity of a mica condenser is not the same for all rates of charge and discharge, and further, that in an alternating current circuit an absorbing condenser behaves as though it were an ideal condenser with non-inductive resistance in series, since the capacity current is out of phase with the electromotive force by less than 90°. For most mica condensers the angle by which the phase differs from quadrature lies in the interval 30″ to 30′ when the frequency is 100 cycles per second.

It may be easily shown that in the comparison of mica condensers of approximately equal capacities by an alternating current bridge method the error introduced by inequality of absorption may be neglected, and as the variation of the capacity of either condenser with the frequency of the alternating current is slight, a change in the ratio of the two capacities may reasonably be expected to be very slight.

The evidence would seem to point to the fact that more reliable comparisons could be made by use of an alternating current bridge than by the so-called bridge method, due to Maxwell, where no especial precautions are taken to remove the galvanometer from the circuit before an appreciable amount of the absorbed charge is released; for Zeleny[2] has recently shown that "the capacity of a mica condenser as determined by the ordinary direct deflection method is a variable quantity and a function of the period of the galvanometer," but that "the capacity determined from the free charge is independent of the period of the galvanometer and dependent on the condenser only."

It has seemed to the writers desirable to make a careful determination of the ratio of two similar condensers employing both the

[1] Bulletin of the Bureau of Standards, No. 3, 1905.
[2] Phys. Rev., No. 2, 1906.

alternating current and the direct (variable) current, under the favorable conditions prescribed by Zeleny, with the purpose of ascertaining whether or not the two methods would give identical results to within the limit of error of about one hundredth of one per cent., which is easily attainable in such determinations.

INSTRUMENTS AND METHOD.

In order that the comparison might be carried out under as nearly similar conditions as possible in the cases of the alternating current and direct current circuits, the same resistance boxes were used in the same positions in both arrangements. These boxes were constructed of manganin wire by Otto Wolff and one of them had been certified by the Reichsanstalt as correct to one part in 10,000. By comparison the other boxes were found to be equally reliable.

The only essential respect in which the alternating current and direct current circuits differed was in the type of galvanometer used, but these were made as nearly similar as the limitations of the problem allowed.

It was thought best to use in both cases a differentially wound galvanometer, as such an instrument may be made practically free of inductance in the state of balance and hence may be shunted with non-inductive resistance with the certainty that the current will divide in inverse proportion to the ohmic resistances of shunt and coil.

The direct current differential galvanometer was a four coil astatic mirror instrument provided with a triple cylindrical soft iron shield to diminish the restoring force of the earth's field. The needles of the astatic system were eight in number and made of tungsten steel. The whole system weighed between four and five milligrams and was supported by a quartz fiber.

Each of the four coils was shaped so as to give nearly maximum field strength for given resistance and was wound with No. 40 silk-insulated copper wire. In winding these coils two strands of the wire were spun around each other and this double wire wound on a frame. Frame and double coil were immersed in hot carnoba wax until the air was expelled from the insulation. When cool the

double coil was slipped off the frame, as it was sufficiently hard to be mounted without a frame in its place in the galvanometer. Each of the four coils of the galvanometer thus consisted of two sets of windings the resistances and inductances of which differed but very slightly. Care was taken in mounting these coils in the galvanometer to pair them off, so that the total resistance of each set of four coils in series was as nearly alike as possible. When the coils were in position the galvanometer consisted of four coils each of which was double, so that there were two circuits through the galvanometer practically coincident along their whole length.

Each of these circuits had a resistance of about 134 ohms and with either set of windings the current sensibility of the instrument as it was finally used was 10^{-9} amperes per mm. deflection at 1^{m} scale distance.

By sending the same current through the two sets of windings so that their magnetic effects on the needle system were in opposition, it was found that if this current were less than 10^{-8} amperes there was no noticeable deflection of the needle. Thus the two systems of windings were symmetrical as regards their magnetic fields, and hence as regards their self-inductions, to within one part in 10,000 which was regarded as satisfactory considering that the effect of a slight asymmetry could be eliminated when it came to the comparison of capacities by the simple expedient of exchanging the two windings. The following scheme of connection will illustrate the method adopted for the comparison of capacities by means of the differential galvanometer.

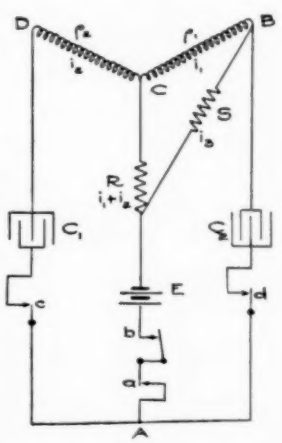


Fig. 1.

ρ_1 and ρ_2 represent the windings of the galvanometer (shown separate in the figure but really coincident and connected so as to oppose in their magnetic effect on the needle system) C_1 and C_2 the capacities to be compared; R and S resistance boxes accurate to 1 in 10,000; a, b, c, d, are keys which are thrown from left to right

(in the figure) by a pendulum in the order a–b and then c and d together. The position of the keys could be varied so as to vary the intervals of time between the falling of the keys. It will be seen from the figure that the circuit is made as the key a falls — is broken later by the falling of the key b and an instant later the keys c and d break the circuit $ABCDA$ through both condensers and the galvanometer coils in series. As the time between the falling of key b and keys c and d was made extremely small (roughly estimated at a few thousandths of a second) this pendulum apparatus secures the charging of the condenser C_1 and C_2 by a common electromotive force E, through the resistances in the branches which respectively contain them.

Calling i_1 and i_2 the instantaneous values of the currents through ρ_1 and ρ_2 the galvanometer will show no deflection on charging the condensers if $i_1 = i_2$.

But $(i_1 + i_2)R + i_1\rho_1 = i_3S$ and

$$i_1\rho_1 + \frac{1}{C_1}\int (i_1 + i_3)dt = i_2\rho_2 + \frac{1}{C_2}\int i_2 dt,$$

but if i_1 is to equal i_2 (ρ_1 being equal to ρ_2) then

$$\frac{1}{C_1}(i_1 + i_3) = \frac{1}{C_2}i_2,$$

but

$$i_3 = \frac{(i_1 + i_2)R + i_1\rho_1}{S}.$$

$$\therefore \frac{1}{SC_1}(S\rho_2 + R\rho_2 + \rho_1\rho_2 + R\rho_1) = \frac{\rho_1}{C_2}$$

or

$$\frac{C_1}{C_2} = \frac{S + \rho + 2R}{S} \qquad \text{Eq. } B$$

since $\rho_1 = \rho_2 = \rho$.

It was found that the balance was not disturbed by changing the relative positions of the keys a and b which shows that the balance point was unaffected by any existing difference in absorption of the two condensers.

The alternating current galvanometer was of the D'Arsonval type

as used by Terry[1] in determining the temperature coefficient of a capacity. In order to make it differential in its action the coil was made of two symmetrical windings of No. 40 wire braided together and with a common terminal leading to the phosphor-bronze upper suspension. There were two lower suspensions of very fine phosphor-bronze attached to the two windings. This method of connection (the use of a common terminal) necessitated an extra half turn on one winding. This half turn could be shifted across the face of the coil until the magnetic effects of the two windings, as tested with direct currents, were balanced to within one part in ten thousand. When used differentially the inductances of the windings were very nearly zero. The field of the galvanometer was of laminated iron with a winding designed to be connected directly to a 110-volt 60-cycle circuit.

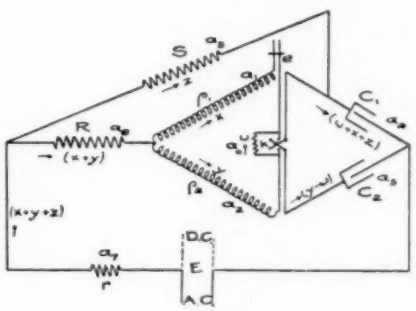


Fig. 2.

This galvanometer may be substituted for the differential telephone or transformer with a great gain in sensibility and in symmetry of windings. For the comparison of capacities the method of connection is that shown in Fig. 2.

The windings ρ_1 and ρ_2 are shown separated. The slide wire l serves to bring the resistances ρ_1 and ρ_2 very nearly to equality. This is determined by a direct current balance with the capacities C_1 and C_2 cut out, and with direct current on the galvanometer field, which is not shown in the sketch. A commutator serves to exchange C_1 and C_2 for the elimination of errors due to asymmetry. These errors were very small. A double pole double throw switch serves to throw 110 volts A.C. or 2 volts D.C. on the circuit. The control resistance K functions exactly as it would in the case of an ordinary A.C. galvanometer, not wound differentially, (Terry. loc. cit.) and hence by its adjustment the coil can be given any desired degree of stability in the alternating field. With respect to

[1] PHYSICAL REVIEW, September, 1905.

the E.M.F. induced in the windings by the alternating field, the resistance K is in series with both windings acting together; but with respect to the measuring current, at the moment of balance K is connected at two points whose potentials are the same. At the moment of balance K carries no part of the measuring current and hence does not necessarily need to be considered in the equation of balance.

This arrangement differs markedly from that used by Trowbridge[1] in the comparison of capacities with the differential transformer only in the use of the resistance R. This gives far more effectiveness to the shunt S, which in turn does not have to be so small when very unequal capacities are compared. Moreover, the sensibility is very nearly the same with a 5:1 ratio of capacities as with an equality balance.

The theory of the network of conductors is given below where u, x, y, z, etc., represent the alternating currents in the various branches, a_0, a_1, etc., the complex expressions for the impedances and E the impressed alternating electromotive force.

Since the self inductions of the coils ρ_1 and ρ_2 of the galvanometer at the instant of balance are just offset by the mutual induction between them as the currents are equal and oppositely directed it is not necessary to include these inductances in the impedances a_1 and a_2.

$$a_1 = \rho_1; \qquad a_3 = \frac{1}{jc_2\omega}; \qquad a_5 = S;$$
$$a_2 = \rho_2 \qquad\qquad a_6 = R;$$
$$a_0 = K; \qquad a_4 = \frac{1}{jc_1\omega}; \qquad a_7 = r.$$

Applying Kirchoff's laws,

$$ya_2 + ua_0 - xa_1 = 0,$$

$$(u + x + z)a_4 + ua_0 - (y - u)a_3 = 0,$$

$$(x + y)a_6 + xa_1 - za_5 = 0,$$

$$(x + y + z)a_7 + za_5 + (u + x + z)a_4 = E.$$

[1] PHYSICAL REVIEW, February, 1905.

Rearranging terms,

$$a_0u - a_1x + a_2y + oz = 0,$$

$$(a_0 + a_3 + a_4)u + a_4x - a_3y + a_4z = 0,$$

$$ou + (a_1 + a_6)x + a_6y - a_5z = 0,$$

$$a_4u + (a_4 + a_7)x + a_7y + (a_4 + a_5 + a_7)z = E.$$

$$u = \frac{1}{\Delta}\begin{vmatrix} O & -a_1 & +a_2 & O \\ O & +a_4 & -a_3 & +a_4 \\ O & +(a_1+a_6) & +a_6 & -a_5 \\ E & +(a_4+a_7) & +a_7 & +(a_4+a_5+a_7) \end{vmatrix}$$

$$= \frac{E}{\Delta}\begin{vmatrix} -a_1 & +a_2 & O \\ +a_4 & -a_3 & +a_4 \\ +(a_1+a_6) & +a_6 & -a_5 \end{vmatrix},$$

$$u = \frac{E}{\Delta}[a_1(a_4a_6 + a_2a_4 - a_3a_5) + a_2a_4(a_5 + a_6)],$$

$$x = \frac{1}{\Delta}\begin{vmatrix} +a_0 & O & +a_2 & O \\ +(a_0+a_3+a_4) & O & -a_3 & +a_4 \\ O & O & +a_6 & -a_5 \\ +a_4 & E & +a_7 & +(a_4+a_5+a_7) \end{vmatrix}.$$

$$= -\frac{E}{\Delta}\begin{vmatrix} a_0 & a_2 & O \\ (a_0+a_3+a_4) & -a_3 & +a_4 \\ O & +a_6 & -a_5 \end{vmatrix}.$$

$$\therefore x = -\frac{E}{\Delta}(a_0a_3a_5 + a_2a_5(a_0 + a_3 + a_4) - a_0a_4a_6)$$

$$y = \frac{1}{\Delta}\begin{vmatrix} a_0 & -a_1 & O & O \\ (a_0+a_3+a_4) & a_4 & O & a_4 \\ O & (a_1+a_6) & O & -a_5 \\ a_4 & (a_4+a_7) & E & (a_4+a_5+a_7) \end{vmatrix}$$

$$= + \frac{E}{\Delta} \begin{vmatrix} a_0 & -a_1 & O \\ (a_0 + a_3 + a_4) & a_4 & a_4 \\ O & (a_1 + a_6) & -a_5 \end{vmatrix}$$

$$y = + \frac{E}{\Delta} [- a_0 a_4 a_5 - a_1 a_5 (a_0 + a_3 + a_4) - a_0 a_4 (a_1 + a_6)].$$

The condition of balance is $x = y$ and a_1 is made $= a_2 = a$,

$$a_0 a_3 a_5 + a_2 a_5 (a_0 + a_3 + a_4) - a_0 a_4 a_6$$
$$= + a_1 a_5 (a_0 + a_3 + a_4) + a_0 a_4 a_5 + a_0 a_4 (a_1 + a_6)$$

$$\therefore \frac{a_3}{a_4} = \frac{a_5 + a + 2a_6}{a_5} \qquad \text{Eq. } A$$

$$\text{or } \frac{C_1}{C_2} = \frac{S + \rho + 2R}{S} \qquad \text{Eq. } B$$

but $u = \frac{E}{\Delta} [a(a_4 a_6 + a a_4 - a_3 a_5) + a a_4 (a_5 + a_6)]$

$$= \frac{Ea}{\Delta} [a_4 (2a_6 + a + a_5) - a_3 a_5]$$

but from Eq. A, $a_3 a_5 = a_4 (a_5 + a + 2a_6)$

$\therefore$ when $x = y$ (a_1 being equal to a_2)

$u = 0$ or no current from the bridge flows through the resistance K.

Under these conditions Eq B gives the value for the ratio of the capacities.

In obtaining the balance both with the alternating current and the direct current circuits, the practice was to exchange the positions of C_1 and C_2 and so obtain a mean value of C_1/C_2 which was free from error due to any slight asymmetry in the apparatus. Of course, the resistance S had always to shunt the circuit through the greater capacity.

The rôle played by the resistance R is evident from the equations or from the diagrams. Its presence slightly reduces the sensibility but on the other hand it makes an accurate knowledge of the resistance ρ less important than as though R were suppressed. This is a great advantage since the galvanometer coils ρ consist of fine

copper wire the resistances of which depend to a considerable extent on the temperature. Moreover, as has been mentioned above, the presence of the resistance R makes the method applicable to the comparison of capacities whose ratio is as great as ten to one.

The above mathematical treatment is of course, applicable to the comparison of inductances. In this case the formula inverts; that is

$$\frac{L_1}{L_2} = \frac{S}{S + 2R + \rho}.$$

In order to avoid taking accurate account of the temperature of the two capacities, we compared the two halves of a subdivided Elliot condenser of one microfarad capacity.

The comparison was made by means of a third Elliot condenser of about one-half microfarad capacity. Furthermore, the work was carried on in a basement room where the variation of temperature did not exceed 7° C., so that on the whole the error introduced by variations of temperature was probably negligible. The formulæ B and B' modify as follows when the ratio $C_1 : C_2$ is obtained by means of the third capacity C_3 which is smaller than either C_1 or C_2.

$$\frac{C_1}{C_3} = \frac{S_1 + 2R_1 + \rho}{S_1} \text{ and } \frac{C_2}{C_3} = \frac{S_2 + 2R + \rho}{S_2}.$$

$$\therefore \left(\frac{C_1}{C_2}\right) = \frac{S_1 + 2R_1 + \rho}{S_2 + 2R_2 + \rho} \times \frac{S_2}{S_1}.$$

When the positions of C_1 and C_2 are exchanged,

$$\left(\frac{C_1}{C_2}\right)' = \frac{S_1' + 2R_1 + \rho}{S_2' + 2R_2 + \rho} \times \frac{S_2'}{S_1'}.$$

It will be seen from Table I. that the observations were taken over a period of about six weeks. They are recorded in the order in which they were taken beginning on April 11 for the comparisons by variable currents, and on April 13 for the comparisons by alternating currents. No observations were discarded, although some of the earlier observations with the alternating current galvanometer were not taken so carefully as were the later ones.

TABLE I.

Comparison by Direct Currents.

Date.	$R=R_2$	S_1	S_1'	S_2	S_2'	$\frac{C_1}{C_2}$	$\left(\frac{C_1}{C_2}\right)'$	Mean $\frac{C_1}{C_2}$
Apr. 11	0	14,100	14,700	8,300	8,500	.9935	.9935	.99350
" 13	0	14,650	11,950	8,500	7,600	.9935	.9936	.99355
" 15	0	15,900	13,000	9,000	7,900	.9936	.9935	.99355
" 17	0	16,050	13,000	9,000	7,950	.9936	.9936	.99360
" 22	0	14,700	12,000	8,600	7,600	.9936	.9936	.99360
" 22	0	14,800	12,050	8,650	7,600	.9937	.9936	.99365
" 23	380	97,500	80,500	57,700	51,600	.9937	.9939	.99380
" 23	380	100,000	82,000	59,000	52,000	.9939	.9938	.99385
" 23	300	84,000	68,200	48,700	43,200	.9937	.9939	.99380
" 24	200	61,000	50,000	35,200	31,200	.9936	.9937	.99365
" 24	150	50,500	41,500	29,200	25,500	.9938	.9936	.99370
" 25	100	42,700	33,500	23,400	20,400	.9937	.9936	.99365
" 25	33	25,300	20,100	13,960	12,150	.9936	.9936	.99360
" 25	333	101,000	80,700	55,200	48,700	.9936	.9935	.99355
" 25	333	100,900	80,500	55,300	48,400	.9936	.9935	.99355
May 27	33	23,200	17,940	13,200	11,300	.9936	.9936	.99360

Average, .99364

Comparison by Alternating Currents.

Date.	$R_1=R_2$	$S_1=S_1'$	$S_2=S_2'$	$\frac{C_1}{C_2}$
Apr. 13	1.5	17,800	10,830	.99400
" 13	1.5	16,768	10,393	.99403
" 14	1.5	16,883	10,273	.99363
" 14	1.5	17,150	10,425	.99375
" 14	1.5	19,600	11,275	.99372
" 14	1.5	20,169	11,619	.99378
" 14	1.5	19,500	11,399	.99372
" 26	1.5	18,475	10,975	.99374
" 26	151.5	50,075	29,475	.99357
" 27	151.5	50,700	29,850	.99369
" 27	151.5	52,100	31,175	.99384
" 27	151.5	50,000	29,750	.99370
" 27	201.5	61,650	36,500	.99373
May 25	1.5	18,204	10,600	.99349
" 25	1.5	18,110	10,650	.99351

Average, .99373

The general averages by the two methods agree to within nine parts in one hundred thousand. Had these averages been made excluding the first few observations, of which we are a little uncertain, they would have been considerably more concordant.

As the check upon the accuracy of the methods we divided the capacity C_2 into two parts of approximately .25 microfarads each, which we will call C_4 and C_5. By comparison with direct currents we determined C_4/C_2 and C_5/C_2 using the above mentioned third capacity C_3. The sum of these ratios should equal C_1/C_2, since $C_4 + C_5 = C_1$. Owing to certain discrepancies which appeared in this portion of the work with the comparison by alternating currents, we shortened the calculations for that method by determining simply C_4/C_3 and C_5/C_3, having previously determined C_1/C_3 which should therefore equal $C_4/C_3 + C_5/C_3$. The value of C_1/C_3 as determined from several averages was 0.98490.

TABLE II.

Comparisons by Direct Currents.

Date.	$\frac{C_4}{C_2}$	$\frac{C_5}{C_2}$	$\frac{C_4}{C_2} + \frac{C_5}{C_2}$	Difference.
April 26	.49623	.49738	.99361	.00003
May 29	.49616	.49736	.99352	.00012
May 30	.49621	.49736	.99357	.00007

Comparisons by Alternating Currents.

Date.	$\frac{C_4}{C_3}$	$\frac{C_5}{C_3}$	$\frac{C_4}{C_3} + \frac{C_5}{C_3}$	Difference.
May 28	.49828	.49910	.99738	.01248
May 28	.49838	.49914	.99752	.01262

It will be seen that for direct currents the agreement is satisfactory, since the differences between $C_4/C_2 + C_5/C_2$ and C_1/C_2 (average from Table I.) are small. The corresponding differences in the case of alternating currents are very large. In order to investigate the cause of these discrepancies another series of observations was taken, of which Table III. is a summary.

TABLE III.

Date.	R_1	R_2	R_3	S_1	S_2	S_3	$\frac{C_1}{C_3}$	$\frac{C_2}{C_3}$	Calc. $\frac{C_4}{C_3} + \frac{C_5}{C_3}$	Obs. $\frac{C_1 + C_2}{C_3}$	Diff.
June 28	1.5	1.5	471.5	18,125	10,885	1,084.3	1.0092	1.0153	2.0245	2.0218	.0027
" 29	1.5	1.5	471.5	18,395	11,010	1,083.5	1.0092	1.0153	2.0245	2.0221	.0023
May 29	301.5	501.5	9001.5	84,750	76,200	18,080.0	1.0091	1.0153	2.0244	2.0134	.0110

The two halves of the subdivided Elliot condenser, C_1 and C_2 were compared with C_3.

Then the whole of the subdivided condenser, $C_1 + C_2$, was compared with C_3.

The results do not check. This was found to be due to distributed capacity in the Wolff box R. An inspection of Table III. shows that consistent values for C_1/C_3 and C_2/C_3 are obtained with values of R varying from 1.5 ohms (the resistance of the upper galvanometer suspension) to 501.5 ohms. A larger variation of R for these ratios is impossible because of the enormous values of S which would accompany high values of R. However, when obtaining $(C_1 + C_2)/C_3$ which is nearly a 2:1 ratio, very large values of R can be used.

It will be seen from Table III that the value of $(C_1 + C_2)/C_3$ is very different when $R_3 = 9001.5$ and when $R_3 = 471.5$. This shows the effect of distributed capacity in R when it is made up of a few coils of high resistance. The difference between computed and observed values of $(C_1 + C_2)/C_3$ increases to nearly five times its previous value. In order to test this point still further a regular capacity bridge was set up (Carhart & Patterson's Electrical Meas.) and it was found that when Wolff boxes were used in the bridge arms a perfect telephonic balance was impossible, on account of distributed capacity in the coils of these boxes.

The position of balance as indicated by a minimum sound in a telephone, or as indicated by an alternating current galvanometer was dependent upon whether the bridge arms consisted of a few high resistance coils or a large number of low ones of exactly the same ohmic resistance. This must be due to the greater distributed capacity in the high resistance coils.

A second curious effect was that a coil possessing distributed capacity, such as a 5,000 ohm coil in a Wolff box, *inserted entirely outside of the bridge circuit*, would affect the point of balance. This may be due to modification of the wave-form by this external distributed capacity, making overtones more pronounced, and thus rendering the distributed capacity in the bridge more effective. This effect was not noticeable unless there was distributed capacity in the bridge as well as in the external circuit.

Both of these effects were far less pronounced when manganin boxes of our own construction were substituted for the Wolff boxes. The coils in the Wolff boxes were wound on brass cylinders, which is an arrangement quite favorable for distributed capacity, while the coils in our own boxes were wound on wooden coils.

Unfortunately these boxes were accurate only to 0.1 per cent., and hence in using these boxes we obtained a check only to within that degree of accuracy. It seems quite clear, however, that the distributed capacity in large values of R, which carries the main current through both capacities, was responsible for the discrepancies noted in the alternating current comparisons.

Moreover, it is quite evident that boxes in which the coils are wound on brass cores, giving considerable distributed capacity are not to be depended on for alternating current measurements of more than moderate precision.

The applied voltage used in the comparisons by means of the differential alternating current galvanometer was varied from 10 to 110 volts at 60 cycles, with no appreciable effect on the results. Hence the varying electrostatic attraction between the condenser plates does not affect the ratio of the parts of the condenser.

A number of tests were made to determine whether distributed capacity in S had any influence on the results. The resistances S were built up first of a few high resistance coils and then of a number of small resistance coils of the same sum total ohmic resistance. No influence upon the results could be detected.

The shunt S carries in most cases so small a current that it was not expected that distributed capacity in it would be troublesome. We have, therefore, reason to believe that the results reported in Table I. are free from the errors due to distributed capacity, since R was small in all cases.

This paper may be summarized as follows:

1. A new circuit for the comparison of capacities and of inductances has been devised, which is more nearly free from errors due to distributed capacity than is the regular Maxwell bridge.

2. Within the limit of error, that is one ten-thousandth, it has been established that the ratio of two good mica condensers is the same, whether compared by direct or by alternating currents, pro-

vided that proper precautions be taken to eliminate the effect of absorption.

3. It has been shown that distributed capacity in high-grade resistance boxes whose coils have brass cores causes a serious error in alternating current measurements; an error which may be much reduced by using boxes whose coils are wound on wooden cores.

MADISON, WIS.,
July, 1906.

AN IMPROVED METHOD OF MEASURING THE INFRA-RED DISPERSION OF MAGNETIC ROTATION; AND THE MAGNETIC ROTATORY DISPERSION OF WATER.

By L. R. Ingersoll.

In a previous article[1] the writer described a bolometric method of measuring the electromagnetic rotation of the plane of polarization of infra-red radiations, if of not too long wave-length. This enabled the determination of the variation of magnetic rotation with wave-length — or the magnetic rotatory dispersion — for a spectral region several times as large in extent as that which could be explored by the customary visual methods. But measurements were difficult, and the several sources of error and rather large corrections to be applied, necessarily detracted somewhat from the certainty of the result.

During the past year, however, a number of radical changes have been introduced, which not only remove in great part the above defects, but also lend to the bolometric method possibilities for sensitiveness in the detection and measurement of minute rotations, considerably exceeding those of visual methods of observation. Hence, as it is believed that the advantage appeals to investigators of making a more thorough study of the magnetic rotatory dispersion of a large class of substances, this improved bolometric method of measurement is described. Results are also given of measurements by its use, of the magnetic rotatory dispersion of water.

The fundamental principle is as already described,[2] and is essentially that due to De la Provostaye and Desains.[3] Light passes in succession through a polarizing agent, through the rotating substance in a magnetic field, and through an analyzer, whose principal

[1] Phil. Mag. (6), 61, p. 41, January, 1906.
[2] Loc. cit.
[3] Ann. Chim. Phys. (3), XXVII., p. 32, 1849.

plane makes an angle of 45° with that of the polarizer. Any rotation of the plane of polarization will cause an increase or diminution of intensity of the light transmitted by the analyzer, which may be measured bolometrically, and for any desired wave-length if the beam is dispersed.

The practical difficulty which must be encountered is that small and unavoidable variations in the intensity of the light source may be falsely interpreted as rotations, and may indeed mask entirely the true effect if it is small. It appeared that it might be possible to overcome this difficulty by utilizing two equal beams from the same source of light, and having them fall eventually on two bolometers, so connected that their currents opposed each other at the galvanometer. For then any variation of intensity of the source would affect both beams equally and produce no resultant deflection, while if only one of the beams was polarized and made to pass through the magnetic field, it alone would suffer changes of intensity due to rotation, and the angle of rotation could be measured as readily as before.

A large number of trials have demonstrated the possibility of compensating in this way for variations of the source, but it has been found that for best results, the two beams should be as nearly identically similar as possible, and that instead of two bolometers, the two strips of a single bolometer may be used to advantage. To fulfill these conditions the following arrangement has been adopted, the general disposition of magnet and mirror system being as before, and as indicated in the diagram of the previous paper.

Light from a Nernst glower, after reflection from a concave mirror and passage through a double image prism and down the axis of the electromagnet, is brought to a focus between the pole-pieces. Only the direct, and therefore achromatic image from the prism is used, hence this prism might be replaced by a Nicol, although the latter, being longer, would cause more absorption. A second mirror converges the beam, after passing through a second double image prism, on a Vierordt double slit. The two images of the source falling vertically above one another on the two halves of the slit, form, after passing through the spectrometer, two slightly separated, and, with the exception of the azimuths of polarization,

entirely similar spectra. These are received on the two strips of a bolometer, so constructed that the strips instead of being side by side, lie vertically over one another. The intensity of either spectrum for any given wave-length may thus be measured by shuttering either half of the slit, — or any relative change of intensity. This last is due to rotation, for, since the plane of polarization of the radiation as it passes between the poles of the magnet makes an angle of 45° with each of the two planes of transmission of the analyzing double image prism, any rotation will cause a diminution of intensity of one image on the slit and a corresponding increase in the other. This change being measured by the bolometer for any given wave-length and divided by the actual intensity of either spectrum for that wave-length, readily gives by the simple computation which will follow shortly, the magnitude of the rotation.

Of the two evident advantages resulting from this arrangement, one has already been mentioned. That is, the differential basis on which the measurement of rotations is placed, whereby the effect of small variations of the light source may be made negligible, and consequently far greater steadiness and certainty in the determination of small rotations secured. The second advantage results from the fact that the effect of any rotation is clearly doubled, since the increase of energy on one bolometer strip is accompanied by an equal decrease on the other, resulting in a doubled galvanometer deflection. Practically the only disadvantage results from the absorption of the calcite double image prisms, which prevents measurement beyond about $\lambda = 2.5\,\mu$. But in very many cases the absorption of the rotating substance itself precludes work beyond this wave-length. In certain other cases, too, particularly that of the magnetic metals, the interesting part of the curve is obtained well within this region of the spectrum, and indeed barely outside the limits of the visible part.

There are, moreover, a number of good features arising from the fact that many of the errors of adjustment, which are almost impossible to avoid, are rendered of negligibly small effect by this arrangement. The reason for this will appear after a brief discussion of the theory of the method.

Let α be the angle which the plane of polarization of the incident

radiation makes with the plane of transmission of the analyzer for the beam which goes to the upper half of the slit. Then if I' represents the intensity for any wave length of the incident beam, the intensities of the two transmitted beams will be:

$$I_1 = k_1 I' \cos^2 \alpha \text{ to the upper half of the slit}$$

and

$$I_2 = k_2 I' \sin^2 \alpha \text{ to the lower half,}$$

where k_1 and k_2 are factors which take account of all losses which may occur to the two beams, due to any cause whatever, *e. g.*, narrowing of either half of the slit, absorption, etc.

Any small rotation of the plane of polarization δ will cause a relative change of intensity for the two beams of

$$dI = 2I'(k_1 + k_2) \sin \alpha \cos \alpha \cdot \delta.$$

Dividing by I, the intensity on either strip of the two are equal, or the mean if they differ slightly,

$$\frac{dI}{I} = 4\delta \frac{(k_1 + k_2) \sin \alpha \cos \alpha}{k_1 \cos^2 \alpha + k_2 \sin^2 \alpha}$$

or,

$$\text{if } \alpha = 45^\circ \; \delta = \frac{1}{4} \frac{dI}{I} \text{ radians or } \frac{45}{\pi} \frac{dI}{I} \text{ degrees.}$$

This shows that if $\alpha = 45^\circ$ a given rotation δ will be indicated by the same value of dI/I whatever the values of k_1 and k_2. Furthermore, $\sin \alpha \cos \alpha$ being a maximum at 45°, a variation even as great as 4° either way changes it by less than 1 per cent, which means a correspondingly small change in the above factor if $k_1 = k_2$. If the two intensities are made equal, as is in general done to secure the compensating action explained above, $k_1 \cos^2 \alpha = k_2 \sin^2 \alpha$, but the change in the factor for a variation in α of several degrees from 45°, is still barely a per cent.

The practical importance of these several facts is, that the factor by which the measured quantity dI/I must be multiplied to give the angle of rotation, is practically a constant unless the variation of α from 45° is unreasonably large. This means that neither small errors

in the adjustment of the polarizing arrangement, nor unknown absorptions or losses of radiation in any part of the apparatus, can have any appreciable effect on the accuracy of the results.

It is of interest to compare the possibilities for accuracy and sensitiveness of this bolometric method of measuring angles of magnetic rotation, with those of the ordinary visual methods. It is evident at once that the relative accuracies of the two will depend very largely on the magnitude of the rotation to be measured. For in ordinary polarimetry, rotations being measured as the difference between two settings of the analyzer, the probable error of the result is practically the same for small as for large rotations. On the other hand, in the present bolometric method, the probable error is by no means constant but is rather a fraction of the whole which is not many times greater for small than for large rotations. It is quite possible then, that, while the accuracy of visual observations may be very considerably greater for relatively large angles of rotation, *i. e.*, of several degrees, the bolometric method may excel in accuracy when the rotation is a hundred times as small.

A few figures will illustrate to what extent this is true. The accuracy of single settings with the most improved form of polarimeter is of the order of .01°. With the ordinary half shade arrangement the writer must confess to frequent discrepancies in successive measurements of several times this amount. On the other hand, in the bolometric method, a rotation of .01° would mean a ratio dI/I of 1:1433 or a galvanometer deflection of one centimeter if the total energy incident on either strip corresponded on the same basis to 1433 cm. This, measured of course with reduced sensibility, is only one-half or one-third of what has readily been secured in practice in parts of the infra-red in the spectrum used, and a much smaller fraction of what would be available if the beam was undispersed. Hence it is evident that rotations several times smaller than could be detected visually, may, under proper conditions, be measured bolometrically. The possibilities for sensibility appear to be limited — supposing a rotating substance of not too great absorption — only by the intensity of the available source of light, and by the success with which this, as well as the bolometer and galvanometer are protected from various disturbing elements.

Of course the two methods are in no sense competitive, applying, as they necessarily do, to entirely different parts of the spectrum but it would seem that the bolometric method might perhaps find a special field of usefulness, outside of its natural application to rotatory dispersion determinations, in the detection of minute rotations. Unfortunately it is not applicable in general to the measurement of rotations due to naturally active substances, save in such a case as Brace's experiment on ether drift, where the effect to be measured is differential. In this case, however, it would probably be difficult to secure a naturally active substance sufficiently transparent in the infra-red to transmit enough energy for the measurements, through the great thickness required.

It is, perhaps, worth noting that the spectrometer and bolometer of this arrangement, taken alone, constitute a type of spectro-photometer applicable to infra-red comparisons of various light sources.

THE MAGNETIC ROTATORY DISPERSION OF WATER IN THE INFRA-RED SPECTRUM.

Verdet[1] measured the magnetic rotation of water in a constant field, for the solar lines, *C* to *G*. Van Schaik[2] extended the determinations into the ultra-violet, finding that the rotation dispersion might be well represented by the expression $a\lambda^{-2} + b\lambda^{-4}$.[3] It was thought desirable in the present case to measure this dispersion for water in the infra-red, both in order to secure determinations for a larger spectral region over which formulæ might be tested, and also to find if the numerous infra-red absorption bands have any appreciable effect in modifying the form of the curve.

Using the foregoing method, measurements were made of the magnetic rotation of water for various infra-red wave-lengths, in a field of approximately 13,000 C.G.S. units. Because of its low rotatory power and high infra-red absorption, it is a peculiarly difficult substance to test in this way, but it was found that by using a rather thin cell — .616 cm. — a fairly consistent series of determinations could be made over the range of spectrum from $\lambda = .7\,\mu$ to $\lambda = 1.3\,\mu$, or as far into the infra-red as the ordinary dispersion has been determined.

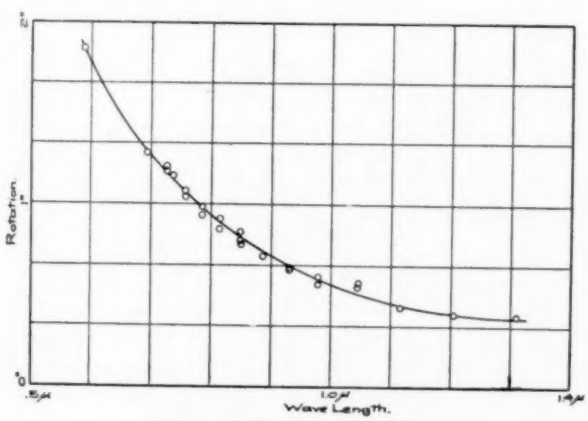
[1] Ann. Chim. Phys. (3), 69, p. 415, 1863. [2] Arch. Néerl., 17, p. 373, 1882.

[3] The careful experiments of Siertsema (Arch. Néerl. (2), 6, p. 825, 1901) give results in fairly good agreement with these.

A detailed description of the magnet and mirror system has already been given [1] and need not be repeated here, as this part of the apparatus was identical with that formerly used. The double image prisms of calcite and glass, used as polarizer and analyzer in the present case, were of 5 cm. and 4.5 cm. aperture, so that a rock salt prism with 8 cm. faces utilized practically the full beam transmitted. The differential bolometer had strips each 8 mm. by .5 mm. It proved in practice an extremely satisfactory instrument, for, as the balancing coils and slide adjustments were contained in the same case as the bolometer itself, "drift" was practically entirely eliminated.

The only correction necessary to the measurements was for the width in the spectrum of the bolometer strip and of the slit image, each .5 mm. wide. This for reasons previously explained,[2] was small, the calculated corrections varying from + 1.5 per cent. at $\lambda = .8\,\mu$ to − 1 per cent. at $\lambda = 1.3\,\mu$. Special tests with a wide slit, giving an exaggerated error, indicated corrections in general accordance with these. The effect of the thin cover glass ends of the cell was safely neglected, since preliminary trials indicated a rotatory dispersion curve for the glass very similar to that for the water, hence the effect of the ends would merely be to increase the equivalent thickness of the water cell 2 or 3 per cent.

In the following curve and table the results are summarized.



Magnetic Rotation of Water.

[1] Loc. cit.

[2] Loc. cit., p. 56.

The rotations plotted in the curve are half those actually measured — since the magnet current is reversed in the measurement — with the small correction above mentioned applied. The observed values given in the table are taken from the smooth curve and reduced to a scale which makes the rotation for sodium light unity. This point was determined by visual observations with a half shade polariscope.

TABLE I.

Wave-length.	Observed Rotations.	Calculated Rotations.	
		(2)	(1)
.589 μ	1.000	1.000	1.000
.70	.695	.676	.683
.80	.514	.496	.510
.90	.389	.389	.399
1.00	.312	.315	.322
1.10	.254	.259	.263
1.20	.220	.220	.220
1.30	.201	.193	.181

The agreement of observed with calculated results is only fair, and hardly as satisfactory as in the case of carbon bisulphide. Results calculated from two slightly different formulæ are given. (1) is with the use of the formula given by Drude.[1]

$$\delta = \frac{1}{n}\left(\frac{a}{\lambda^2} + \frac{b\lambda^2}{(\lambda^2 - \lambda_1^2)^2}\right)$$

where $\lambda_1 = .127\,\mu$ is the wave-length of an ultra-violet absorption band. The constants, being determined for wave-lengths $.589\,\mu$ and $1.2\,\mu$ give $a = -.176$ and $b = +.582$, (2) uses the same formula modified by a term depending on the infra-red absorption band having its maximum at $\lambda = 3.02\,\mu$.

$$\delta = \frac{1}{n}\left(\frac{a'}{\lambda^2} + \frac{b'\lambda^2}{(\lambda^2 - \lambda_1^2)^2} + \frac{c'\lambda^2}{(\lambda^2 - \lambda_2^2)^2}\right).$$

The constants, determined for wave-lengths $.589\,\mu$, $.9\,\mu$ and $1.2\,\mu$ are $a' = -.517$; $b' = +.890$; $c' = +.804$.

It will be observed that there is only questionable advantage in

[1] Lehrbuch der Optik, p. 403.

favor of the second formula, which assumes the influence of an infra-red absorption band. This might perhaps be anticipated from the fact that the ordinary dispersion curve for water as determined by Rubens[1] as far as $\lambda = 1.256\,\mu$, does not show the effect of such an absorption band — in the early infra-red at any rate.

It is of interest to note that the theoretical formula proposed by Becquerel[2] and further worked out by Larmor,[3]

$$\delta = \varkappa\lambda \frac{dn}{d\lambda},$$

which fits very well in the case of carbon bisulphide,[4] fails entirely here, giving values for the rotation several times too large at $\lambda = 1.3\,\mu$.

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[1] Wied. Ann., 45, p. 253, 1892.

[2] Comptes Rendus, Nov., 1897.

[3] Ether and Matter, p. 353.

[4] A discussion of this formula in its application to carbon bisulphide was unfortunately omitted in the previous paper. However at the suggestion of Professor Larmor it has since been tried and found to apply very well to $\lambda = 2.0\,\mu$ which is as far as the ordinary dispersion has been determined.

THE IRREVERSIBILITY OF THE HEUSLER ALLOYS.

BY BRUCE V. HILL.

A LITTLE over a year ago the author, while making some experiments upon specimens of Heusler's magnetic bronzes (of manganese, copper and aluminium) found that these alloys are magnetically irreversible, but in a sense opposite to the irreversibility of the nickel-steels. A brief account of these experiments was published in this journal.[1] If an alloy of iron and nickel, containing up to twenty-seven per cent. of nickel, in the magnetic condition, be heated to from 700° to 750°C. it becomes unmagnetic. On being cooled it does not regain its susceptibility until the temperature has fallen to a point considerably below, in some cases several hundred degrees below, that at which the transformation took place during the heating. When heated a second time the metal remains magnetic until the original temperature of transformation is reached. If, starting at a high temperature with the steel in the unmagnetic condition, we descend to a moderate temperature, reheat to the starting point, cool again to a temperature lower than that reached in the first cooling, reheat and so on, we find that the susceptibility of the metal will, in general, be greater at room temperature, the lower the point to which it has been cooled.

With the magnetic bronzes, on the other hand, cooling to low temperatures, as in liquid air, has very little effect. The susceptibility depends rather upon the temperature from which the specimen has been cooled before the test is made. If heated to a temperature slightly above that of transformation, the susceptibility at room temperature is found to be smaller than when the alloy was first cast. On cooling successively from still higher temperatures the susceptibility at ordinary temperatures increases as the temperature from which the metal has been cooled rises.

It was further pointed out that, inasmuch as certain compounds

[1] PHYSICAL REVIEW, 21, p. 335, 1905.

of manganese possess a higher susceptibility than the corresponding ones of iron, we might expect to obtain the former in a strongly magnetic condition if a suitable alloy could be obtained. The magnetic bronzes are such alloys.

According to the allotropic theory, which seems to be pretty well established, the ferromagnetic metals can exist in several allotropic forms depending upon the temperature. Only one of these forms is magnetic. In the case of many of the mechanical and physical properties, it is impracticable to study a substance at temperatures much above the ordinary. An indirect method must then be employed. When a metal is heated to a high temperature and suddenly cooled, passing in so doing a point of allotropic transformation, this transformation which would have occurred during a slow cooling, is hindered or perhaps almost wholly prevented by the rapid cooling. This is made use of in studying the conditions existing in alloys at high temperatures. In the case of the steels, for example, when the metal has been heated to a high temperature and suddenly cooled, we consider that we have it before us in the condition in which it was at the high temperature. If this were strictly true in all cases we might expect to find the magnetic bronzes magnetic at high temperatures since their susceptibility is greater the more elevated the temperature from which they have just come. Without experiment it is impossible to say whether this will be true or not. We naturally think of these metals as being always unmagnetic above the temperature of transformation. Dr. D. K. Morris found, however, that iron becomes unmagnetic at a temperature between 700° and 750°C, but regains its susceptibility to a slight extent between 800° and 1,000°C. I thought it worth while therefore to test some further specimens of the Heusler alloy in order to determine the magnetic condition of the metal between the points of transformation and fusion, that is between 250° and 1,000°C.

Four alloys were prepared. They were made by melting a copper-manganese alloy with aluminium. An ordinary gasoline furnace was used and the melts made under borax glass as a flux. The copper-manganese was obtained from one of the best firms in the country and was supposed to contain thirty per cent. of man-

ganese. The upper portion of the pig of metal contained a considerable amount of slag. The analyses showed the per cent. of aluminium to be so nearly that of the mixture before melting, while that of the manganese was so much below what was expected, that it is fair to assume that the manganese was burned out in the manufacture of the original copper-manganese alloy. The analyses, for which I am indebted to Professor McFarland of the Department of Chemistry of the University of Kansas, are as follows:

Alloy Number.	Copper.	Aluminium.	Manganese.
1	74	22	4
2	65	34	1
3	65	32.5	2.5
4	63	34.3	2.7

The discoverer of these bronzes, F. Heusler[1] has recently published an account of experiments upon certain alloys rich in copper which are, nevertheless, very highly magnetic and which are malleable.

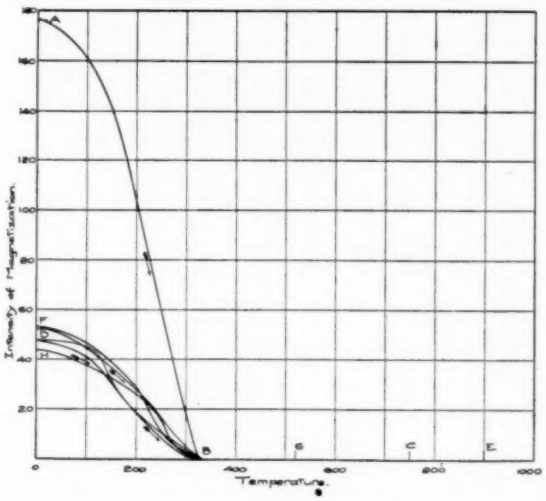
The apparatus used in the testing of my alloys was that described in the previous note upon this subject. The temperatures were measured with a platinum — platinum 10 per cent. rhodium couple. The curves showing the relation between the intensity of magnetization and the temperature for alloy No. 1 during three successive cycles are given in the figure. The field throughout the tests was 38 C.G.S. units. The curves of decreasing intensity, that is of increasing temperature, are indicated by the arrows immediately below them.

Starting at room temperature the intensity, I, is 175. It falls rapidly as the temperature rises, becoming zero at 320°C. The heating was continued up to 750°, the point C in the figure. On cooling the curve returns to the point D where $I = 47$. The tem-

[1] F. Heusler, Beiblaetter, 29, 1238, 1905, or Schriften d. Marburger Gesell. J. A. Fleming and R. A. Hadfield have published tests upon some of these alloys but nothing distinctly new is given.

Professor A. Gray, of Glasgow (Proc. Roy. Soc., Sect. A., 77, p. 256, March 6, 1906), has also tested two specimens of these bronzes finding them like those of the other experimenters.

perature was now raised to 890°C., the point *E*. This time the return was to *F*, $I = 53$. Being heated the third time to 520°C. and cooled to room temperature the rod showed an intensity $I = 44$.



Alloy No. 2 was unmagnetic as cast. Pounding or jarring produced no noticeable effect. The rod was then heated successively to 325°, 490° and 810° C., but it remained unmagnetic throughout. When broken in a mortar the fragments were magnetic. It melted at 975° C.

Alloy No. 3 showed a course similar to that of No. 1. When cast the intensity, *I*, was 123. Transforming at 300° it was heated to 320° and allowed to cool. *I* attained a value of 128. The second heating was to 500°, after which the intensity at room temperature was 48. The third heating was to 730°, after which the value of *I* was 41. The fourth heating was to 890°, the intensity becoming $I = 44$ at room temperature.

Alloy No. 4 was tested at room temperature as cast and after being heated to the same series of temperatures as was No. 2. The results were: As cast $I = 41$, after heating to 325° $I = 41$, after heating to 490° $I = 14$ and after heating to 810° $I = 63$.

The data for these four alloys, as well as for the one described in the previous paper, which will be called No. 5, are brought together in the table. $H = 38$ for the first four and 85 for the fifth.

Alloy No. 1	As cast	520°	750°	890° C.	
	$I = 175$	44	47	53	
Alloy No. 2	As cast	325°	490°	810° C.	
	$I = 0$	0	0	0	
Alloy No. 3	As cast	320°	500°	730°	890° C.
	$I = 123$	128	48	41	44
Alloy No. 4	As cast	325°	490°	810° C.	
	$I = 41$	41	14	63	
Alloy No. 5	As cast	368°	500°	650°	850° C.
	$I = 311$	267	27	90	155

From these results we see that, in general, the susceptibility of the alloy at room temperature decreases as the temperature to which it has been heated rises, up to a certain point, beyond which the intensity increases again. Nos. 4 and 5 show these characteristics more pronouncedly than the others. All the alloys, with the possible exception of No 3 in the first cycle, show them however, though in the first four, those of low manganese content, they are not so marked.

We see also from the figure that the alloys do not regain their magnetic properties at the higher temperatures. If we assume that the molecular state of the metal is in great measure that naturally stable at the higher temperature due to the retardation or non-occurrence of certain allotropic changes, then we must suppose that there are different molecular arrangements of the metals constituting the alloy at different temperatures. The relations existing at high temperatures allow the transformation of the manganese from the *beta* to the *alpha* state to take place more completely than in those molecular groupings existing at lower temperatures. The temperature-intensity cycles are irreversible, but cannot be repeated as with the irreversible nickel-steels. This is probably due, in part at least, to the fact that the time during which the metal is held at a certain temperature plays a great part in determining the nature of its subsequent properties, as shown originally by Messrs. Haupt and Stark [1] and by E. Gumlich [2]. By casting a number of rods from the same crucible, and thus avoiding the repeated heating of the same rod, some additional information might be gained.

[1] Marburger Schriften, Bd. 13, 1904.
[2] Ann. d. Phys., 16, p. 535, 1905.

While the experiments upon these bronzes may have brought us very little nearer to an understanding of the phenomenon of magnetism, they seem to make it evident that we have here to do with a molecular and not an atomic property.

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NOTE ON THE VIBRATION GALVANOMETER.

BY ROY T. WELLS.

IN Annalen der Physik, Bd. 4, Heft 3, March, 1901, p. 439, Max Wien described an apparatus very considerably more sensitive than a telephone, for the detection and measurement of harmonic electromotive forces and currents of small amplitude.

The writer sometime since had occasion to investigate with such an instrument

(*a*) Its accuracy of tuning, that is the variation of its amplitude of motion when acted upon by an electromotive force of constant amplitude and frequency, the natural period of the instrument being varied from less than to more than that of the impressed electromotive force.

(*b*) The way in which the magnitude of the instrumental reading varies with the amplitude of an impressed electromotive force of fixed frequency, with which it is in resonance.

An electrically driven tuning fork was arranged to open and close a circuit consisting of battery and coil of wire, giving an intermittent, unidirectional current in the coil. A second coil in inductive relation to the first thus had induced in it an alternating electromotive force, and was connected in series with a piece of German silver wire stretched along a scale, there being accordingly a non-harmonic alternating current in the stretched wire, of almost perfectly fixed frequency.

(*a*) The galvanometer terminals were kept connected to certain fixed points of the stretched wire, so that when the galvanometer key was closed a constant current passed through its coil. The free length of the suspending wire was varied by small increments and the corresponding amplitude of vibration noted.

The results are given in Table I. and plotted in Fig. 1, the variables in each case being free length of wire in centimeters and amplitude of vibration as measured on a scale in the eyepiece of the observing telescope.

From the table it is seen that for this wire and frequency a free length of wire of 11.94 cm. brought the needle into resonance with the impressed electromotive force. From the amplitudes with free lengths of 11.90 and 11.94 cm. it is seen that a reduction of the free length of .34

TABLE I.

Free Length.	Amplitude.	Free Length.	Amplitude.
10.16	2.750	12.95	6.875
10.41	2.750	13.21	6.875
10.67	4.125	13.46	5.500
10.92	4.125	13.71	5.500
11.18	2.750	13.96	4.125
11.43	4.125	14.13	4.125
11.69	6.875	14.23	4.125
11.90	8.250	14.40	5.500
11.94	137.500	14.58	4.125
12.19	13.750	14.75	4.125
12.45	10.800	15.13	4.125
12.70	8.250		

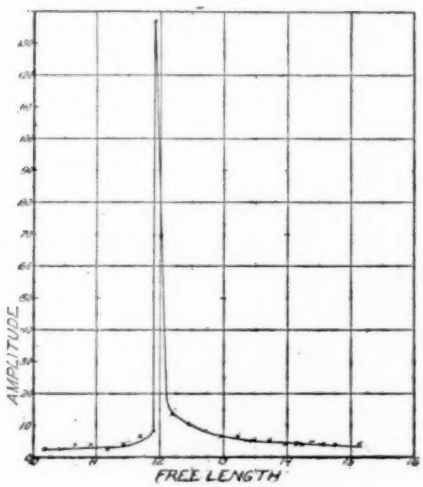

Fig. 1.

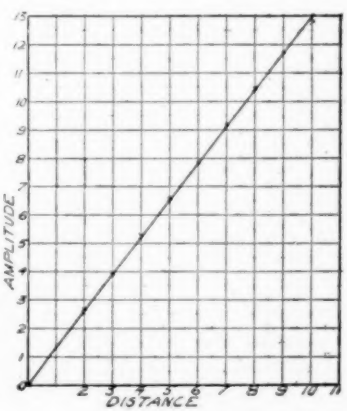

Fig. 2.

per cent. and hence a reduction of .17 per cent. in the natural period of the needle reduces the amplitude of vibration by 90 per cent. This shows that to use such an instrument satisfactorily it must be accurately tuned and supplied with an electromotive force almost perfectly constant in frequency.

(*b*) The instrument was tuned to the tuning fork, and its terminals connected to points on the stretched wire at distances apart increasing by regular increments, the amplitude of vibration being noted in each case. The results are given in Table II. and plotted in Fig. 2, the variables in

each case being distance in centimeters between points of galvanometer connection and amplitude of vibration.

TABLE II.

Distance.	Amplitude.	Distance.	Amplitude.
1	1.32	6	7.84
2	2.68	7	9.16
3	3.93	8	10.48
4	5.30	9	11.71
5	6.58	10	12.80

These results show that the amplitude of vibration is very closely proportional to the impressed potential difference.

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NEW BOOKS.

Ions, Electrons, Corpuscles. Memoires reunis et publié par HENRI ABRAHAM et PAUL LANGEVIN. Paris, Gautier-Villars, 1905. Pp. xvi + 1138.

This important collection of papers, which constitutes the second series of memoirs issued by the *Société Française de Physique*, deals, as the title indicates, with the phenomena upon which the modern conception of the existence and function of the electrified particle is based. The charged corpuscle has become a fundamental quantity in our newer theories concerning matter and electricity and the contributions gathered together and rendered easily available in this compilation represent an important epoch in physics.

The work was originally undertaken on behalf of the Société de Physique by the late Professor Potier and to his memory the present volume is dedicated by its editors Professors Abraham and Langevin.

The literature of this new portion of the science of physics is already so large as to compel the exclusion, even from so voluminous a collection as this, of many papers of interest and significance. While some readers will regret the entire omission of the work of various contributors to our knowledge, as for example that of Barus and of Child, every one will be glad that place was found for the early papers of such pioneers as Plücker, Hittorf, Crookes, Coulier, Giese and Hertz.

In these days when men of science, whatever their nationality, make daily use of English, French and German in about equal proportions it would seem as though all of the papers of this collection might well have been reprinted in the original. The foreign memoirs have however been rendered into French and the surprising skill of the French scientific translator, which often enables him to preserve the thought of an author and to give it a more complete and perfect expression is pleasingly manifest in the various versions prepared by M. M. Langevin, Salles, Bloch, Gallotti, Benard, Buirson, Lugol and Moulin. The very important summary of the work of Lorentz was prepared by the author himself.

In preference to either the chronological order or the arrangement of material according to subjects, the editors have placed the various papers alphabetically by authors, a plan awkward for the few who may wish to read the work through consecutively but which greatly facilitates the use of the collection as a book of reference.

E. L. N.

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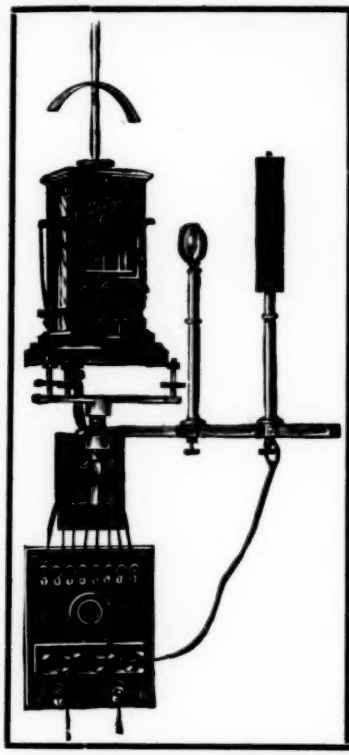

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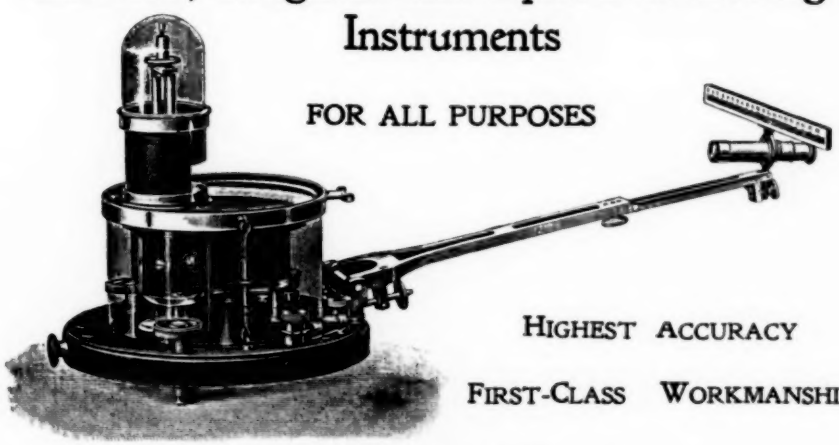

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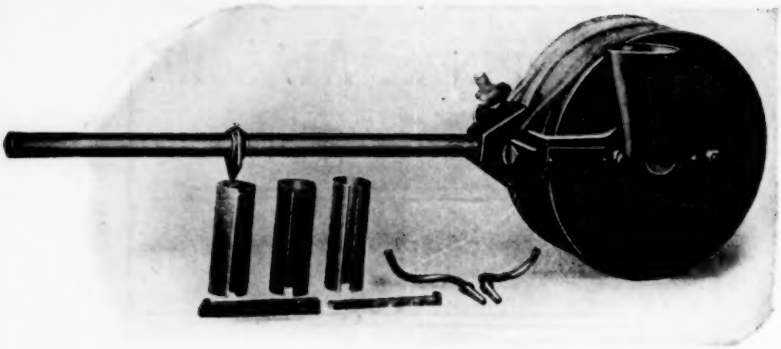

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